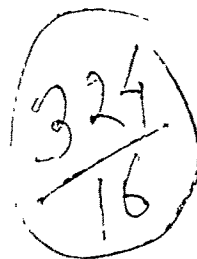


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## MOLECULAR REARRANGEMENT OF SOME *O*-ACYLOXYACYLARONES IN PRESENCE OF METALLIC SODIUM

BY SHARAD S. PANDIT AND SURESH SETHNA

The triacetate and the tribenzoate of phloracetophenone and the diacetates and dibenzoates of quinacetophenone, respropiofenone and resbutyrophenone have been subjected to molecular rearrangement in presence of metallic sodium in dry toluene. The acetates on molecular rearrangement gave the known chromone derivatives and the benzoates, the known flavone derivatives except in the case of resbutyrophenone dibenzoate where only benzoic acid was isolated

Baker (*J. Chem. Soc.*, 1933, 1381) observed that *o*-aroyloxyacylarones could be transformed to *o*-hydroxydiaroylmethanes by means of potassium carbonate. These  $\beta$ -diketones could then be transformed into chromones and flavones by dehydration. A number of reagents have been found to bring about this rearrangement. Mahal and Venkataraman (*ibid.*, 1934, 1767) found sodamide to be effective. Virkar and Wheeler (*ibid.*, 1939, 1679) observed that metallic sodium in dry toluene or dry ether could bring about the same rearrangement. They also found that by using metallic sodium molecular rearrangement of resacetophenone diacetate and 4-*O*-benzoyl-2-*O*-acetyiresacetophenone, which could not be carried out by the use of potassium carbonate, could be effected and that it provided a convenient process for the synthesis of 2-naphthylchromones, nitroflavones and 2-alkylchromones. Virkar (*J. Univ. Bombay*, 1942, 11, III, 136) and Virkar and Shah (*ibid.*, 1942, 11, III, 140; *Proc. Ind. Acad. Sci.*, 1949, 30A, 57) have subjected a number of *o*-acyloxyacetoarones to this rearrangement in presence of metallic sodium. Ullal, Shah and Wheeler (*J. Chem. Soc.*, 1940, 1499) found that alcoholic sodium ethoxide also brought about the same rearrangement at room temperature.

Though a large number of *o*-acyloxyacetoarones have been subjected to molecular rearrangement, the acetates and benzoates of the two simple ketones, quinacetophenone and phloracetophenone, have not been subjected to this rearrangement. Further, the work done so far has been restricted to *o*-acyloxyacetoarones and no work has been carried out on the *o*-acyloxypropiofenones and *o*-acyloxybutyrophenones. The triacetate and the tribenzoate of phloracetophenone and the diacetates and dibenzoates of quinacetophenone, respropiofenone and resbutyrophenone have therefore been subjected to this molecular rearrangement in presence of metallic sodium, as this reagent has been found by Virkar *et al.* (*loc. cit.*) to give the best results.

Phloracetophenone triacetate and tribenzoate on molecular rearrangement gave the known 5:7-dihydroxy-3-acetyl-2-methylchromone and 5:7-dihydroxy-3-benzoylflavone respectively. Quinacetophenone diacetate and dibenzoate gave the known 6-hydroxy-3-acetyl-2-methylchromone and 6-hydroxyflavone respectively. Respropiofenone diacetate and dibenzoate gave the known 7-hydroxy-2:3-dimethylchromone and 7-hydroxy-3-methylflavone respectively and resbutyrophenone diacetate gave the known 7-hydroxy-2-methyl-3-ethylchromone. In the case of resbutyrophenone dibenzoate only benzoic acid could be isolated from the reaction mixture. The intermediate  $\beta$ -diketones could not be isolated in any of these rearrangements.

The mechanism for the formation of simple and 3-acylchromones from the *o*-acyloxyacylarones in this rearrangement is very likely the same as that given by Baker (*loc. cit.*) for the formation of chromones when an *o*-hydroxyacylarone is heated with the anhydride and the sodium salt of a fatty acid

The work on the diacetates and the dibenzoates of respropiofenone and resbutyrophenone provides some data regarding the effect of the acyl group other than the acetyl in this rearrangement. The only other data available of this nature are the molecular rearrangements of 2-phenylacetyl-1-naphthylcinnamate and 2-phenylacetyl-1-naphthylacetate which were found to undergo transformations into 2-styryl-3-phenyl-1:4- $\alpha$ -naphthapyrone and 2-methyl-3-phenyl-1:4- $\alpha$ -naphthapyrone respectively in presence of soda-mide (Bhalla, Mahal and Venkataraman, *J. Chem. Soc.*, 1935, 868).

#### EXPERIMENTAL

*Molecular Rearrangement of Phloracetophenone Triacetate: 5:7-Dihydroxy-3-acetyl-2-methylchromone.*—Phloracetophenone triacetate (6 g.), prepared according to Gulati, Seth and Venkataraman (*J. Chem. Soc.*, 1934, 1766), was dissolved in dry toluene (25 c.c.) and was added to pulverised sodium (0.8 g.). The reaction mixture was refluxed for 4 hours between 120° and 130° in an oil-bath. At the end of that period the unreacted sodium was dissolved in alcohol and the reaction mixture was filtered. The residue consisting of the sodium salt was decomposed with dilute acetic acid and the 5:7-dihydroxy-3-acetyl-2-methylchromone obtained was crystallised from dilute alcohol in reddish prisms (1.75 g.), m.p. 251°. (Found: C, 61.4; H, 4.1. Calc. for  $C_{12}H_{10}O_4$ : C, 61.4; H, 4.3 per cent). This was deacetylated to 5:7-dihydroxy-2-methylchromone by heating with 10% sodium carbonate solution. The product obtained was crystallised from dilute alcohol in dark yellow plates, m.p. 278°. Gulati, Seth and Venkataraman (*loc. cit.*) who obtained these chromones in their work on the Kostanecki acetylation of phloracetophenone give m.p. 252° and 279° respectively for the two products.

*Molecular Rearrangement of Phloracetophenone Tribenzoate: 5:7-Dihydroxy-3-benzoylflavone.*—Phloracetophenone tribenzoate, prepared from phloracetophenone by the Schotten-Bauman method, was crystallised from rectified spirit in pink needles, m.p. 118°. Canter, Curd and Robertson (*J. Chem. Soc.*, 1931, 1248) give m.p. 117°. The tribenzoate (4 g.), dissolved in dry toluene (25 c.c.), was added to pulverised sodium (0.8 g.) and the reaction mixture was heated for 4 hours at 120°-130° in an oil-bath and the 5:7-dihydroxy-3-benzoylflavone, obtained on working up the reaction mixture as before, was crystallised from dilute alcohol in pale pink needles (2.1 g.), m.p. 143-44°. (Found: C, 68.3; H, 4.4. Calc. for  $C_{17}H_{12}O_6$ : C, 68.8; H, 4.5 per cent).

The 3-benzoylflavone was debenzoylated to 5:7-dihydroxyflavone by boiling with 10% sodium carbonate solution. The product obtained was crystallised from dilute alcohol in reddish prisms, m.p. 273°. Trivedi, Sethna and Shah (*this Journal*, 1943, 20, 172) who obtained these products in their work on the Kostanecki-Robinson benzoylation of phloracetophenone, give m. p. 145-46° and 275° respectively for the two compounds.

*Molecular Rearrangement of Quinacetophenone Diacetate: 6-Hydroxy-3-acetyl-2-methylchromone.*—Quinacetophenone, prepared according to Amin and Shah (this *Journal*, 1948, **25**, 381) was converted into its diacetate by heating with acetic anhydride and pyridine. The diacetate on crystallisation from alcohol gave white needles, m.p. 68°. Klinger and Kolvenbach (*Ber.*, 1898, **31**, 1216) give the same m.p.

Quinacetophenone diacetate (4 g.) was heated with pulverised sodium (0.3 g.) in dry toluene (20 c.c.) for 6 hours at 120°-130°. The product obtained on working up as usual gave from absolute alcohol pale brown needles (0.92 g.), m.p. 215°. This product was directly compared with an authentic specimen of 6-hydroxy-3-acetyl-2-methylchromone, prepared by the Kostanecki acetylation of quinacetophenone according to Desai and Mavani (*Proc. Ind. Acad. Sci.*, 1947, **26A**, 354) who give m.p. 221° for this product. It was deacetylated to 6-hydroxy-2-methylchromone, m.p. 252°, by boiling with sodium carbonate solution. Desai and Mavani (*loc. cit.*) give the same m.p.

*Molecular Rearrangement of Quinacetophenone Dibenzoate: 6-Hydroxyflavone.*—Quinacetophenone dibenzoate was prepared by benzoylating quinacetophenone with benzoyl chloride and pyridine. It was crystallised from dilute alcohol in pale brown needles, m.p. 113°. Klinger and Kolvenbach (*loc. cit.*) give the same m.p.

Quinacetophenone dibenzoate (4 g.) was heated with pulverised sodium (0.8 g.) in dry toluene (60 c.c.) for 4 hours at 120°-130°. On working up the reaction mixture 6-hydroxyflavone was obtained. It was crystallised from dilute alcohol in light yellow prisms, m.p. 231°. (Found: C, 75.2; H, 4.6. Calc. for  $C_{15}H_{10}O_3$ : C, 75.6; H, 4.2 per cent). Chadha and Venkataraman (*J. Chem. Soc.*, 1933, 1075), who obtained it in their work on the benzoylation of quinacetophenone, give m.p. 234°. Kostanecki, Levi and Tambor (*Ber.*, 1899, **32**, 331) give m.p. 231-32°.

*Molecular Rearrangement of Respropiophenone Diacetate: 7-Hydroxy-2: 3-dimethylchromone.*—Respropiophenone was prepared from resorcinol by the application of Hoesch's method according to Canter, Curd and Robertson (*J. Chem. Soc.*, 1931, 1262). Its hitherto unknown *diacetate* was prepared by heating respropiophenone (4 g.) with acetic anhydride (12 c.c.) and a few drops of pyridine for 4 hours. The oil obtained on pouring the reaction mixture into ice and hydrochloric acid was taken up in ether and washed with dilute alkali and water. The oil obtained on removal of ether gave no coloration with alcoholic ferric chloride. This was distilled under reduced pressure but the distilled product gave characteristic coloration with ferric chloride. The product, however, was almost insoluble in alkali indicating that the decomposition was slight. However, for the purposes of analysis and rearrangement the washed oil, which did not give any coloration, was dried under reduced pressure at 100° and then used. (Found: C, 62.5; H, 5.7.  $C_{13}H_{14}O_3$  requires C, 62.4; H, 5.6 per cent).

Respropiophenone diacetate (3 g.), dissolved in dry toluene (30 c.c.), was added to pulverised sodium (0.6 g.). The reaction mixture was heated for 4 hours at 120°-130°. On working up the reaction mixture 7-hydroxy-2: 3-dimethylchromone was obtained which was crystallised from rectified spirit in pale green needles (0.67 g.), m.p. 262°. (Found: C, 69.6; H, 5.7. Calc. for  $C_{11}H_{10}O_3$ : C, 69.5; H, 5.3 per cent). Canter, Curd and Robertson (*loc. cit.*) who prepared it by the Kostanecki acetylation of respropiophenone, give m.p. 265°.

*Molecular Rearrangement of Respropiofenone Dibenzoate. 7-Hydroxy-3-methylflavone.*—The hitherto unknown *respropiofenone dibenzoate* was prepared from *respropiofenone* (3 g.), dissolved in pyridine and benzoyl chloride (4.5 c.c.). The reaction mixture was heated on a water-bath for 3 hours and then poured in ice and hydrochloric acid. The solid separating was washed with sodium bicarbonate solution and then with water and it was crystallised from dilute alcohol in fine orange colored needles (4.5 g.), m.p. 88-89°. (Found: C, 73.9; H, 4.8.  $C_{23}H_{18}O_3$  requires C, 73.8; H, 4.8 per cent).

*Respropiofenone dibenzoate* (2 g.), dissolved in dry toluene (30 c.c.), was added to pulverised sodium (0.4 g.) and the reaction mixture heated in an oil-bath at 120°-130° for 4 hours. On working up the reaction mixture 7-hydroxy-3-methylflavone was obtained. It was crystallised from dilute alcohol in pale cream colored plates (0.23 g.), m.p. 278°. (Found: C, 76.2; H, 4.8. Calc. for  $C_{16}H_{12}O_3$ : C, 76.2; H, 4.4 per cent). Canter, Curd and Robertson (*loc. cit.*), who prepared it by benzylation of *respropiofenone*, give the same m.p.

*Molecular Rearrangement of Resbutyrophenone Diacetate: 7-Hydroxy-3-ethyl-2-methylchromone.*—*Resbutyrophenone* was prepared according to Brewster and Harris (*J. Amer. Chem. Soc.*, 1930, 52, 4869) from resorcinol, butyric acid and zinc chloride. The hitherto unknown *resbutyrophenone diacetate* was prepared by refluxing *resbutyrophenone* (5 g.), acetic anhydride (20 c.c.) and a few drops of pyridine. On pouring it in ice and dilute hydrochloric acid a liquid separated which was taken up in ether. The ether extract was washed with sodium bicarbonate solution. On removal of ether viscous liquid remained which was distilled, b.p. 170°-175°/15 mm. Slight decomposition seemed to take place during distillation as the distilled product though insoluble in alkali gave reddish coloration with alcoholic ferric chloride. (Found: C, 63.3; H, 6.6.  $C_{11}H_{16}O_6$  requires C, 63.6; H, 6.1 per cent).

*Resbutyrophenone diacetate* (4 g.), dissolved in dry toluene (30 c.c.), was added to pulverised sodium (0.8 g.) and heated for 4 hours at 120°-130°. The reaction mixture on working up as usual gave 7-hydroxy-3-ethyl-2-methylchromone which was crystallised from rectified spirit in pale greenish blue needles (0.8 g.), m.p. 238° (Found: C, 71.1; H, 6.2.  $C_{12}H_{12}O_4$  requires C, 70.6; H, 5.9 per cent). Canter, Curd and Robertson (*loc. cit.*) who prepared it by the Kostanecki acetylation of *resbutyrophenone*, give the same m.p.

*Attempted Molecular Rearrangement of Resbutyrophenone Dibenzoate.*—The hitherto unknown *resbutyrophenone dibenzoate* was prepared from *resbutyrophenone* (5 g.), dissolved in sufficient pyridine and benzoyl chloride (15 c.c.). The reaction mixture was heated on a boiling water-bath for 3 hours. On working up the reaction mixture as usual an oily liquid separated which was distilled, b.p. 210°/25 mm. (Found: C, 74.1; H, 4.9.  $C_{24}H_{20}O_3$  requires C, 74.2; H, 5.2 per cent). When *resbutyrophenone dibenzoate* was subjected to molecular rearrangement under different conditions of reaction the only product which could be isolated was benzoic acid.

The thanks of the authors are due to Dr. R. C. Shah for his kind interest in this work.

## PERIODIC ACID AND PERIODATES. THE TERNARY SYSTEM SILVER OXIDE — PERIODIC ACID — WATER AT 0°.

By P. P. GYANI

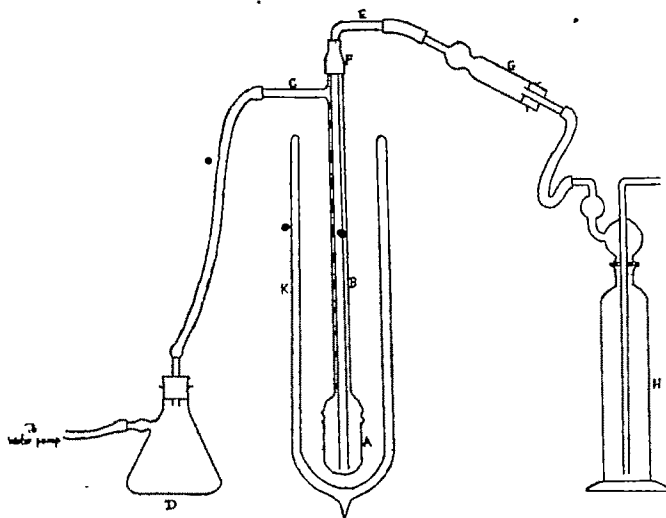
The reaction between silver oxide and periodic acid in presence of water only has been quantitatively studied at 0°. Three distinct salts, viz  $5\text{Ag}_2\text{O} \cdot \text{I}_2\text{O}_7$ ,  $2\text{Ag}_2\text{O} \cdot \text{I}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$  and  $\text{Ag}_2\text{O} \cdot \text{I}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$  are found to be formed. Some properties of these compounds are recorded. The first two have been isolated in a pure condition.

While studying the 35° isotherm of the ternary system silver oxide-periodic acid-water (appearing elsewhere) it was observed that the compound  $2\text{Ag}_2\text{O} \cdot \text{I}_2\text{O}_7 \cdot \text{H}_2\text{O}$ , which is red, did not form immediately on mixing suitable proportions of the three components. Instead, a straw-yellow powder was obtained which required over 24 hours to change into the red compound. This was at first suspected to be due to the action of light, specially in view of the fact that silver salts were involved. Subsequent experiments, however, showed that this was not the case. The change occurred in the dark also. It was therefore considered useful to study the system at a lower temperature, 0°, at which the straw-yellow compound was stable.

### EXPERIMENTAL

With comparatively dilute solutions of periodic acid the arrangement shown in Fig. 1 was used. A was an elongated bulb of pyrex glass carrying a long stem B

FIG. 1



and a side-tube C. The capacity of the bulb was about 100 c.c. and it was made somewhat irregular in shape to break up froth. C was attached to a guard vessel D which

in turn was joined to a water pump. An inner tube E of pyrex glass nearly reached the bottom of the bulb and was attached to it by means of a piece of rubber tubing F. To E were attached in series a soda-lime tube G and a washbottle H containing sulphuric acid. The bulb B was kept in a Dewar vessel K packed with crushed ice. The mixtures to be studied were made up by taking varying proportions of the three components. The mixtures were introduced into the bulb one at a time. On starting the pump a current of  $\text{CO}_2$ -free, dry air was drawn through the bulb which served to keep the mixture thoroughly agitated. After allowing sufficient time for equilibrium to be attained (3 or 4 days), the solid was allowed to settle. The saturated solution and the wet residue were then analysed as described in previous papers (*loc. cit.*).

With mixtures containing a large excess of periodic acid (which necessitated the use of smaller volumes of water) the arrangement used was that employed for the determination of solubility of periodic acid in water at  $0^\circ$ . The mixture was introduced into a small bulb and sealed as before prior to mechanical shaking (cf. Gyani and Gyani, *this Journal*, 1949, **26**, 239).

The results of the analyses of the various saturated solutions and the corresponding wet residues are given in Table I. The first column gives the amount of  $\text{Ag}_2\text{O}$  and the second that of the acid calculated as  $\text{I}_2\text{O}_7$ , for the solution. The next two columns give the corresponding amounts in the wet residue. The amount of acid has been expressed in terms of  $\text{I}_2\text{O}_7$ , for reasons given in the previous paper.

TABLE I

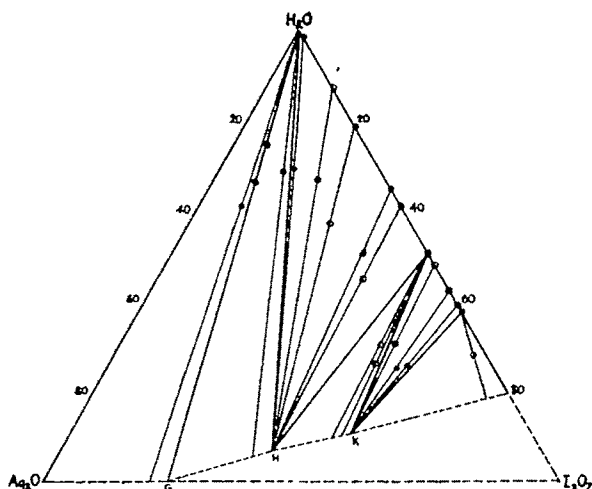
*Silver oxide-periodic acid-water at  $0^\circ$ .*

Percentages by weight				
Solutions		Wet residues		Solid phase
Ag <sub>2</sub> O.	I <sub>2</sub> O <sub>7</sub> .	Ag <sub>2</sub> O.	I <sub>2</sub> O <sub>7</sub> .	
Traces	Traces	31.28	8.15	Ag <sub>2</sub> O + 5Ag <sub>2</sub> O.I <sub>2</sub> O <sub>7</sub>
„	0.0235	19.70	6.32	5Ag <sub>2</sub> O.I <sub>2</sub> O <sub>7</sub>
„	0.0252	25.82	8.27	
0.0016	0.0306	19.09	12.88	5Ag <sub>2</sub> O.I <sub>2</sub> O <sub>7</sub> + 2Ag <sub>2</sub> O.I <sub>2</sub> O <sub>7</sub> .3H <sub>2</sub> O
0.0025	1.321	17.00	14.16	2Ag <sub>2</sub> O.I <sub>2</sub> O <sub>7</sub> .3H <sub>2</sub> O
0.0039	13.07	13.34	20.31	
0.0064	21.87	15.96	27.67	
0.0175	35.48	12.76	37.03	
0.0236	39.13	15.77	39.76	
0.0456	49.71	19.29	50.48	2Ag <sub>2</sub> O.I <sub>2</sub> O <sub>7</sub> .3H <sub>2</sub> O + Ag <sub>2</sub> O.I <sub>2</sub> O <sub>7</sub> .4H <sub>2</sub> O
0.0463	49.73	22.46	51.79	
0.0398	52.11	16.71	53.11	Ag <sub>2</sub> O.I <sub>2</sub> O <sub>7</sub> .4H <sub>2</sub> O
0.0409	57.77	18.96	56.29	
0.0203	60.95	16.47	57.93	
Traces	62.53	2.33	69.75	Ag <sub>2</sub> O.I <sub>2</sub> O <sub>7</sub> .4H <sub>2</sub> O + I <sub>2</sub> O <sub>7</sub> .5H <sub>2</sub> O
—	62.51	—	—	I <sub>2</sub> O <sub>7</sub> .5H <sub>2</sub> O

## DISCUSSION

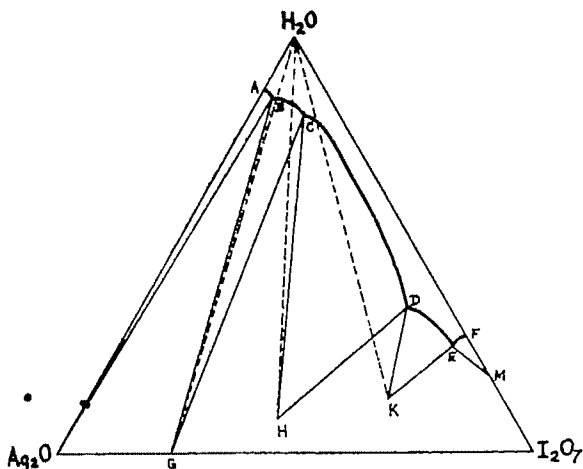
The results obtained in the above experiments are shown graphically in Fig. 2.

FIG 2



It will be observed that the ternary saturation curves of the different solid phases lie so close to the  $\text{H}_2\text{O}-\text{I}_2\text{O}_7$  edge of the diagram that they practically coincide with it. Fig. 3 expresses the same results but has been drawn out of proportion so as to make the different saturation curves distinguishable. Thus, for example, the point A representing the saturated solution of  $\text{Ag}_2\text{O}$  in water should occur very close to the  $\text{H}_2\text{O}$ -vertex but has been shown considerably removed from it. Besides the ternary saturation curves AB and EF for  $\text{Ag}_2\text{O}$  and  $\text{I}_2\text{O}_7$  respectively, which are far too small to be experimentally realised, there are three more curves in Fig. 3, namely, BC, CD and DE. The curve BC, points on which represent solutions containing between 0.00 and 0.0306%  $\text{I}_2\text{O}_7$ , is also small and corresponds to a solid binary compound whose composition is represented by the formula  $5\text{Ag}_2\text{O} \cdot \text{I}_2\text{O}_7$  (point G in Fig. 3). Curve CD, which extends between 0.0306 and 49.72%  $\text{I}_2\text{O}_7$ , is the saturation curve for the ternary compound  $2\text{Ag}_2\text{O} \cdot \text{I}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$  represented by the point H. Curve DE, which lies in a still more acidic region, namely, between 49.72 and 62.51%  $\text{I}_2\text{O}_7$ , that is, up to the saturation point of periodic acid, corresponds to a ternary compound,  $\text{Ag}_2\text{O} \cdot \text{I}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$  (point K).

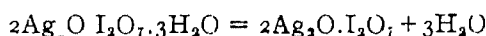
FIG. 3



The compound  $5\text{Ag}_2\text{O} \cdot \text{I}_2\text{O}_7$  is the same as that obtained at  $35^\circ$ . The compound  $2\text{Ag}_2\text{O} \cdot \text{I}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$  is a straw yellow powder. The compound  $\text{Ag}_2\text{O} \cdot \text{I}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$  is a white crystalline solid.

The compound  $5\text{Ag}_2\text{O} \cdot \text{I}_2\text{O}_7$  was found to be stable in contact with water as was the case at  $35^\circ$ . It was therefore readily obtained in a pure state. Analysis of the compound confirmed its composition.  $2\text{Ag}_2\text{O} \cdot \text{I}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$  is not stable in contact

with water the reason for which is clear from Fig 3. For the isolation of this compound advantage has, however, been taken of the fact that it is capable of existence in contact with a very dilute solution of periodic acid, whose concentration is represented by the point C, namely, a solution containing 0.03%  $I_2O_7$  (cf.  $2Ag_2O \cdot I_2O_7 \cdot H_2O$  at  $35^\circ$ ). The compound  $2Ag_2O \cdot I_2O_7 \cdot 3H_2O$  was therefore washed with a solution of this particular strength obtained by washing a little of the compound  $2Ag_2O \cdot I_2O_7 \cdot 3H_2O$  till the solid phase contained a mixture of this compound and  $5Ag_2O \cdot I_2O_7$  at  $0^\circ$ . It was dried over  $CaCl_2$  at  $0^\circ$  and analysed. (Found:  $Ag_2O$ , 52.15;  $I_2O_7$ , 41.16.  $2Ag_2O \cdot I_2O_7 \cdot 3H_2O$  requires  $Ag_2O$ , 52.47;  $I_2O_7$ , 41.41 per cent) The compound  $Ag_2O \cdot I_2O_7 \cdot 4H_2O$ , as can be seen from Fig 3, is capable of stable existence only in contact with very concentrated solutions of periodic acid. The isolation of this compound is therefore difficult, more so, because it has a tendency to change on slight elevation of temperature. The compound  $2Ag_2O \cdot I_4O_7 \cdot 3H_2O$ , when heated in an air-oven at  $105^\circ-110^\circ$ , at first turned black and then gradually became chocolate. The total loss of weight on heating was 7.77%, while dehydration according to the equation



requires a loss of 6.12%. It is interesting to note that the difference of 1.55% between the observed and calculated values is of the same order as observed in the case of the compound  $2Ag_2O \cdot I_2O_7 \cdot H_2O$ , namely, 1.65%.

The properties of the different compounds obtained at the two temperatures are conveniently summarised in Table II.

TABLE II

No.	Formula	Physical properties.	Stability.
1.	$5Ag_2O \cdot I_2O_7$ ( $Ag_5IO_6$ ?)	Black crystalline solid	Stable both at $0^\circ$ and $35^\circ$ Stands washing with water. Can be obtained pure and dry.
2.	$2Ag_2O \cdot I_2O_7 \cdot H_2O$ ( $Ag_4I_2O_3 \cdot H_2O$ ?)	Shining chocolate crystals	Stable at $35^\circ$ in contact with dilute periodic acid containing 0.07 to 50% $I_2O_7$ .
3.	$Ag_2O \cdot I_2O_7$	Canary-yellow crystals	Stable at $35^\circ$ in contact with periodic acid containing over 50% $I_2O_7$ . On washing it changes into (2) then into (1). Stable at $0^\circ$ in contact with acid solutions containing about 1 to 40% $I_2O_7$ . On washing it changes into (1). At $35^\circ$ it changes into (2)
4.	$2Ag_2O \cdot I_2O_7 \cdot 3H_2O$	Straw-yellow powder	
5.	$Ag_2O \cdot I_2O_7 \cdot 4H_2O$	Colorless crystals	Stable at $0^\circ$ in contact with acid solutions containing over 52% $I_2O_7$ . With slight elevation of temperature it changes into (3).

Further work on these compounds is in progress.

In conclusion the author wishes to thank Professor B. P. Gyani whose constant help and guidance made this work possible. The author is also grateful to the Patna University for the award of a research scholarship and to the authorities of the Science College for providing all the facilities for work.



## ELECTROLYTIC PREPARATION OF COPPER ARSENATE

By D. SINGH AND T. R. SIVARAMAKRISHNAN

The preparation of copper arsenate has been carried out by electrolysing a neutral solution of sodium arsenite in a diaphragm cell between copper anode and iron cathode. The influence on its production of the following parameters were studied: Sodium arsenite concentration, C.D., duration of electrolysis, addition of cerous oxide and temperature. The current efficiency under optimum conditions has been observed to be 60%.

Copper arsenate has been prepared from time to time by various chemical methods (Mellor, "A Comprehensive Treatise on Theoretical and Inorganic Chemistry", Vol. IX, p. 157); the products are usually contaminated with several impurities due to the formation of a large number of intermediate products. The possibilities of the electrolytic process have, however, not been hitherto investigated in adequate details in the field of copper arsenate preparation. But a review of literature shows that a series of investigations on the electrolytic preparation of sodium arsenate (Lowenstein, *Trans. Electrochem. Soc.*, 1929, **76**, preprint, **8**, 29; Essin, *Z. Elektrochem.*, 1929, **35**, 234), calcium arsenate (Lloyd and Kennedy, *Chem. Met. Eng.*, 1925, **32**, 624) and lead arsenate (Ormont, *Chem. J. Ukraine*, 1926, **2**, 10) have been carried out by the oxidation of sodium arsenite using suitable anodes. In the present investigation an attempt has therefore been made to synthesise copper arsenate by the electrolysis of aqueous sodium arsenite solution using copper anodes.

### EXPERIMENTAL

The experiments were carried out in a diaphragm cell; it consists of a glass jar and a porous pot of capacities 1.5 and 1.0 litres respectively. The cell was kept immersed in a thermostat maintained at the desired temperature within  $\pm 0.5^\circ$ . The anode used was a thin rectangular sheet ( $8.0 \times 5.0$  cm.) of copper and cathode, a thick iron plate ( $8.0 \times 5.0 \times 0.5$  cm.). The catholyte in all cases was 3.0 g. of sodium nitrate dissolved in 300 c.c. of water.

Since the electrolysis was carried out in absolute neutral medium, the product of electrolysis in all cases was usually a bluish green precipitate containing copper arsenite and arsenate. In all estimations 0.2 g. of the precipitate was dissolved in hot dilute sulphuric acid and titrated against a standard potassium permanganate solution and the amount of copper arsenite was calculated. A second sample of 0.2 g. of the product was dissolved in about 20 c.c. of the acid and the requisite amount of sodium hydroxide solution was added to precipitate completely copper as copper hydroxide. The precipitate was filtered, washed well and dried. Finally it was weighed as copper oxide after incineration and thus the total amount of copper was computed. The filtrate contained both sodium arsenite and arsenate which was boiled with excess of concentrated hydrochloric acid and the arsenic was estimated gravimetrically by precipitating

completely as arsenious sulphide. Thus the total quantity of arsenic was obtained and the quantity corresponding to arsenate content was determined. Copper arsenite is soluble in ethyl alcohol, whereas arsenate is insoluble, and the separation of the product was therefore carried out by using this solvent. In each experiment 1.0 g. of the mixture was taken, shaken well with the alcohol and filtered through a Gooch crucible. The residue was dried and weighed. Thus the amount of copper arsenate was determined. Each estimation was carried out at least twice. The mean value was invariably in agreement with those observed analytically.

The optimum concentration (cf. curve  $C_1$ , Fig. 1) and time (cf. curve  $C_3$ , Fig. 1) have been arrived at empirically.

To investigate the further optimum conditions for the production of copper arsenate the influence of the following factors was studied :

- (a) Current density (curve  $C_2$ , Fig. 1).
- (b) Addition of cerous oxide (curve  $C_4$ , Fig. 1).
- (c) Temperature (curve  $C_5$ , Fig. 1).

The anolyte in the following experiments contained 3 g. of sodium nitrate dissolved in 500 c.c. of water together with 12.5 g. of sodium arsenite neutralised by acetic acid. The potential difference across the cell was maintained at 25 volts.

*Experiments on the Effect of Current Density.*—Electrolysis was continued for  $\frac{1}{2}$  hour at  $28^\circ$ . Results are plotted in curve  $C_2$ , Fig. 1.

*Experiments on the Effect of Cerous Oxide.*—Electrolysis was continued for 2 hours at  $28^\circ$  and at C. D. of 2.5 amp./dm<sup>2</sup>. Results are plotted in curve  $C_4$ , Fig. 1.

*Experiments on the Effect of Temperature.*—Cerous oxide (0.5 g.) was added to the experimental electrolyte and electrolysis continued for 2 hours at a C.D. of 2.5 amp./dm<sup>2</sup>. Results are plotted in curve  $C_5$ , Fig. 1.

The  $p_H$  of the anolyte remains constant during the electrolysis, whereas that of the catholyte varies from 7.0 to 11.1 at the optimum condition.

## DISCUSSION

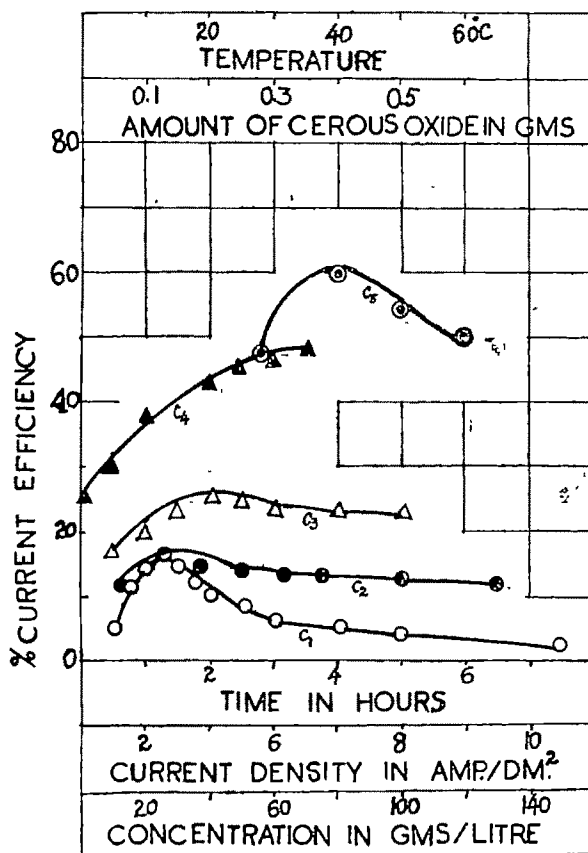
Curves (Fig. 1) show the influence of various parameters in the production of copper arsenate. It is observed that the copper arsenite is formed preferentially to copper arsenate in absence of an oxygen carrier, since the solution potential of copper and the oxidation potential of sodium arsenite are very close to each other.

Results (cf. curve  $C_1$ , Fig. 1) show that the current efficiency is low (4.09%) at a concentration of 10 g. of sodium arsenite/litre probably due to the lack of depolariser, sodium arsenite which consequently leads to much evolution of oxygen. The current efficiency increases with increase of concentration and reaches its maximum (16.69%) at 25 g./litre. Above this approximate concentration it decreases steadily due to the excess of depolariser which helps the formation of copper arsenite and subsequently lessens the yield of arsenate.

Data shown in curve  $C_3$ , Fig. 1 tend to prove the fact that in electrolytic oxidations, the potential for oxygen evolution is reached at relatively low current densities. A high concentration of depolariser opposes concentration polarisation and keeps down the

anode potential, whilst a high current density has the opposite effect. With C.D. of 2.5 amp./dm<sup>2</sup>, the current efficiency reaches a maximum (16.69%). At higher C.D.s

FIG. 1



the efficiency decreases due to much current being wasted in discharging oxygen and hydrogen at the anode and cathode. Below C.D. 2.5 amp./dm<sup>2</sup>, the efficiency falls possibly due to the decrease in oxygen overvoltage and much current being wasted in discharging oxygen.

The effect of duration of electrolysis is generally of considerable importance in all oxidation processes. Oxygen overvoltage increases towards a maximum value and then, in some cases, shows a slight decrease on continued electrolysis. This is actually exhibited in the case of copper arsenate (cf. curve C<sub>3</sub>, Fig. 1). At 30 minutes the yield is low (16.7%) and gradually increases with time due to rise in oxygen overvoltage and reaches a maximum at about 2.0 hours. With the further progress of electrolysis the efficiency decreases gradually.

Not only the material of the electrode but also additions to electrolyte, can act as catalysts in anodic oxidations. Some of these oxygen carriers viz., cerous oxide, cerous sulphate are very important. The salts can readily be oxidised anodically to ceric one, powerful oxidising agents, which react readily with so many reducing substances

converting them smoothly and quantitatively into single oxidation products. The compound thus obtained will be reoxidised, the result of the whole operation being the quantitative oxidation of the depolariser (Allmand and Ellingham, "The Principles of Applied Electrochemistry", 2nd Ed., p. 105). So the effect of cerous oxide on the production of copper arsenate was studied (cf. curve C<sub>1</sub>, Fig. ). It is evident that the current efficiency steadily increases with the increased addition of cerous oxide and reaches 47.19% with 0.5 g. of the oxide.

The influence of an increase of temperature on an anodic oxidation during the evolution of oxygen may act favourably by increasing the velocity of diffusion of the depolariser; it may also lower the oxygen overvoltage and consequently facilitate the oxidation of the depolariser. It would be thus better to carry on the work at a high or a low temperature in accordance with one or other of these two effects predominates. At a certain temperature the arsenate formation is favoured and consequently the current efficiency and the yield per K. W. H. increase and at others they diminish appreciably. Thus in the electrolytic preparation of copper arsenate the best results are obtained at 40° (cf. curve C<sub>6</sub>, Fig. 1).

The authors' thanks are due to Prof. S. S. Joshi, for suggesting the problem and for his keen interest and valuable guidance during the course of this investigation.

ELECTROCHEMISTRY SECTION,  
CHEMICAL LABORATORIES,  
HINDU UNIVERSITY, BANARES.

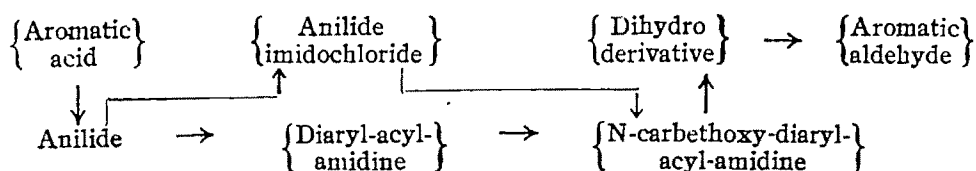
*Received August 24, 1949.*

## A NEW METHOD FOR CONVERSION OF AROMATIC CARBOXYLIC ACIDS INTO THE CORRESPONDING ALDEHYDES. PART I

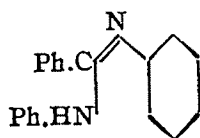
BY M. V. SHIRSAT AND R. C. SHAH

Ghadiali and Shah's (this *Journal*, 1949, 26, 117) new method for conversion of aromatic carboxylic acids into the corresponding aldehydes through N:N'-diphenyl-N-carbethoxybenzamidine has been systematically studied in detail in case of conversion of benzoic acid into benzaldehyde. Of the two alternative methods used by them for the preparation of N-carbethoxy-N,N'-diphenylbenzamidine, the action of ethyl chloroformate on diphenylbenzamidine has been found to be more convenient. This method has now been used for reduction of a number of aromatic acids to the corresponding aldehydes, through the corresponding N-carbethoxybenzamidines. The reactions at various stages were found to be quite smooth giving good yields and the method appears to be of general applicability for aromatic acids.

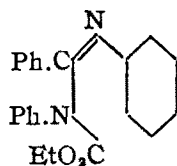
Ghadiali and Shah (this *Journal*, 1949, 26, 117) observed that N:N'-diphenyl-N-carbethoxybenzamidine (II) could be reduced by aluminium amalgam in moist ether to a dihydrobenzamidine (III) which readily hydrolysed by cold dilute acid to benzaldehyde. This important observation affords a convenient method for the conversion of an aromatic carboxylic acid into the corresponding aldehyde (Ghadiali, Shirsat and Shah, *Curr. Sci.*, 1948, 17, 332).



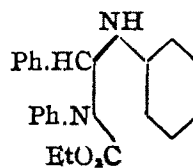
In the present investigation the new method of Ghadiali and Shah (*loc. cit.*) has been systematically studied in case of the conversion of benzoic acid into benzaldehyde. Benzoic acid through its anilide was converted into N:N'-diphenyl-N-carbethoxybenzamidine (II) by two methods (cf. Ghadiali and Shah, *loc. cit.*): (1) through the condensation of benzanilide imidochloride with sodium salt of phenylurethane, and (2) through the action of ethyl chloroformate on N:N'-diphenylbenzamidine (I) obtained by the condensation of benzanilide with aniline (Shah and Sidiki, *J. Univ. Bombay*, 1937, 6A, 136).



(I)



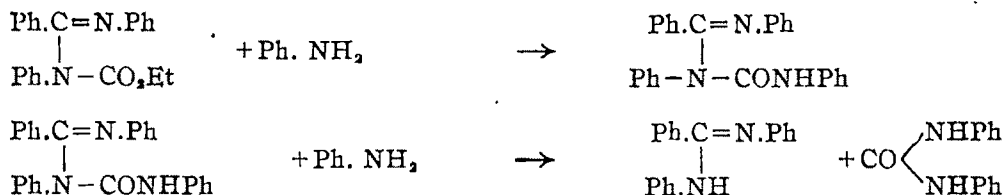
(II)



(III)

In the latter condensation of *N:N'*-diphenylbenzamidine with ethyl chloroformate, a reaction first studied by Ghadiali and Shah, it was observed that the reaction could be successfully conducted in dry ether or in dry acetone as a solvent.

Ghadiali and Shah (*loc. cit.*) prepared *N:N'*-diphenyl-*N*-carbethoxybenzamidine (II) for the first time and studied its reactions. Some more reactions of it have now been studied. It was observed that the compound could be distilled under reduced pressure without decomposition. Ghadiali and Shah who attempted distillation at ordinary pressure observed that it decomposed to *N:N'*-diphenylbenzamidine. An attempt to prepare a picryl derivative resulted in the formation of aniline picrate. An attempt to condense the compound with aniline with a view to obtaining *N*-(phenyliminobenzyl)-*N:N'*-diphenylurea (cf. Ichaporia and Shah, *J. Chem. Soc.*, 1936, 431) resulted instead in the formation of *N:N'*-diphenylbenzamidine and *sym*-diphenylurea. The result may be explained by assuming that the desired condensation product, probably formed in the reaction mixture, further reacts with one more mole of aniline to give rise to these two products.



Sidiki and Shah (*loc. cit.*) who condensed *N:N'*-diphenyl-*N*-carbethoxycinnamidine with aniline obtained only *sym*-diphenylurea.

The *N*-carbethoxybenzamidine (II) could easily be reduced to *N:N'*-diphenyl-*N*-carbethoxydihydrobenzamidine (III) by aluminium amalgam using moist ether or preferably moist ethyl acetate as a solvent. The reductions with stannous chloride in dry ether or metallic sodium in absolute methyl alcohol were unsuccessful. The dihydro compound (III) was found to be highly unstable, being easily hydrolysed to aldehyde on heating with water or preferably in dilute hydrochloric acid. Even during the reduction some dihydro compound got hydrolysed giving benzaldehyde. An attempt at benzoylating the dihydrobenzamidine resulted in the formation of benzaldehyde and benzanilide, while one at acetylation resulted in its hydrolysis to benzaldehyde and phenylurethane.

As out of the two above methods of conversion, the one through *N:N'*-diphenylbenzamidine and its *N*-carbethoxy derivative was found to be more convenient, it was applied for conversion of several substituted benzoic acids into the corresponding aldehydes.

Thus, *o*-chlorobenzoic acid through *o* chlorobenzanilide was converted into *N:N'*-diphenyl-*o*-chlorobenzamidine, which condensed with ethyl chloroformate to give *N:N'*-diphenyl-*N*-carbethoxy-*o*-chlorobenzamidine. The latter on reduction with aluminium amalgam and subsequent hydrolysis of the *dihydrobenzamidine* obtained, furnished *o*-chlorobenzaldehyde; *meta*- and *para*-bromobenzoic acids through *N:N'*-diphenyl-*m*- and *p*-bromobenzamidines gave the corresponding *N*-carbethoxybenzamidines. On

reduction the *m*-bromobenzamidine gave a *dihydro* product which hydrolysed to the aldehyde. The *p*-bromobenzamidine derivative, however, gave directly *para*-bromobenzaldehyde, the dihydrobenzamidine being not isolated.

Similarly the anilides of *o*-, *m*- and *p*-toluic acids gave through the respective *N:N'*-diphenyltoluamidines the corresponding *N*-carbethoxytoluamidines. The *o*- and *m*-toluamidines on reduction gave directly the aldehydes; while the *para* derivative furnished the *dihydro*toluamidine which hydrolysed to give *p*-tolualdehyde.

In all these cases of conversion, the reactions at various stages were found to be quite smooth giving good yields and the method appears to be of general applicability for aromatic acids.

#### EXPERIMENTAL

*N:N'*-Diphenyl-*N*-carbethoxybenzamidine (II).—(i). Sodium salt of phenylurethane (from 5 g. sodium and 26 g. of phenylurethane) was refluxed with benzanilide imidochloride (30 g.) in dry ether for 12 hours according to Ghadiali and Shah (*loc. cit.*). The reaction product obtained as a yellow paste did not solidify and hence it was distilled under reduced pressure. The fraction at 230°-250°/20 mm. could be crystallised from a mixture of benzene and light petroleum in prismatic needles, m.p. 86-87°, yield 12 g. (Ghadiali and Shah, *loc. cit.*, m.p. 85-87°).

(ii). To a solution of *N:N'*-diphenylbenzamidine (I) (1 g., 1 mol.) in dry benzene (10 c.c.) was added ethyl chloroformate (0.4 g., 1 mol.) dissolved in dry benzene (1 c.c.) with cooling in a freezing mixture and the reaction mixture kept overnight at 0°. It was filtered and on removal of benzene from the filtrate a yellow paste was obtained which was washed with light petroleum (60°-80°) and the solid obtained crystallised from alcohol, m.p. 86°, yield 0.6 g.

Similar results were obtained by using sodium bicarbonate as used by Ghadiali and Shah. It was also observed that replacement of benzene by dry acetone did not affect the yield, while use of higher temperatures diminished the yield.

Reactions of *N:N'*-Diphenyl-*N*-carbethoxybenzamidine (II).—(i). The benzamidine (II) could be distilled undecomposed at 220°/3 mm. (cf. Ghadiali and Shah, *loc. cit.*).

(ii). An attempt to prepare a picrate of the benzamidine (II) in hot alcoholic solution resulted in the formation of aniline picrate, m.p. 189-90°, hydrolysis having taken place.

(iii). The benzamidine (II, 1.5 g.) and aniline (1 g.) were heated at 180° for 4 hours, when the reaction product on crystallisation from alcohol gave *sym*-diphenylurea (carbanilide), m.p. 238-39° and *N:N'*-diphenylbenzamidine (I), m.p. 141°.

Reduction of *N:N'*-Diphenyl-*N*-carbethoxybenzamidine (II) to *N:N'*-Diphenyl-*N*-carbethoxydihydrobenzamidine (III). Aluminium amalgam.—The usual method

given in literature did not give satisfactory results, hence it was prepared as follows : Aluminium wire (0.05 cm. dia., 7.0 g.) was cut into pieces of about 8 to 10 cm. in length, and each piece rolled into a small coil. They were then washed with ether, acetone and water; treated with sodium hydroxide solution (5%) for about two minutes and then with hydrochloric acid (5%) and finally washed with plenty of water. After thorough washing, the coils dipped in water (10 c.c.) were treated with solid mercuric chloride (1 g.) and the flask shaken with cooling if necessary. When all the mercuric chloride went in solution more water was added and then the contents washed. Most of the water was decanted off keeping about 10 c.c. and mercuric chloride (1 g.) was again added and the process repeated twice, till the aluminium coils were coated with sufficient amount of mercury. The coils were thoroughly washed with water till free of mercuric chloride, then with ether and directly used.

To a freshly prepared aluminium amalgam (16 g.) a solution of N:N'-diphenyl-N-carbethoxybenzamidine (II, 2 g.) in moist ether (alcohol-free ether to which were added 2 or 3 drops of water, 200 c.c.) was added. The amalgam reacted vigorously liberating tiny bubbles of hydrogen. After 20 minutes, the solution was filtered and the ether distilled off. The solid that remained was crystallised from a mixture of petroleum and benzene as colorless glistening needles, m.p.  $103^{\circ}$ , yield 1.5 g. (Ghadiali and Shah, *loc. cit.*, m.p.  $104-106^{\circ}$ ).

Similar yields were obtained when moist ethyl acetate was used as a solvent; the reduction being more vigorous in this case, the reaction period was only 15 minutes.

The original benzamidine (II) was recovered unchanged when the reduction was attempted with stannous chloride in ethereal suspension and passing hydrogen chloride under anhydrous conditions. Attempted reduction of the benzamidine (II) in methyl alcoholic solution by metallic sodium resulted in the formation of N:N'-diphenylbenzamidine (I).

*Reactions of N:N'-Diphenyl-N-carbethoxydihydrobenzamidine (III).* (i) *Hydrolysis*.—The dihydrobenzamidine (2 g.) was treated with concentrated hydrochloric acid (5 c.c.), well stirred and a further quantity of dilute hydrochloric acid (30 c.c.) added. It was well shaken, warmed on a water-bath, cooled and extracted with ether. The ether extract was dried, ether removed and the brownish oil (0.4 g.) that remained was identified as benzaldehyde by preparing its 2:4-dinitrophenylhydrazone, m.p. and mixed m.p. with one prepared from benzaldehyde,  $258^{\circ}$  (Curtius and Dedischen, *J. prakt. Chem.*, 1894, ii, 50, 264, give m.p.  $235^{\circ}$ ).

(ii). Attempted benzoylation of the dihydrobenzamidine (0.5 g.) by benzoyl chloride (1 c.c.) in a solution of sodium hydroxide (10%, 5 c.c.) gave benzanilide, m.p.  $160^{\circ}$ , and benzaldehyde.

(iii). Attempted acetylation of the dihydrobenzamidine (0.5 g.) with fused sodium acetate (0.4 g.) and acetic anhydride (1 c.c.) by heating on a water-bath for half an hour gave phenylurethane, m.p.  $52^{\circ}$  (after crystallisation from light petroleum, b.p.  $60^{\circ}-80^{\circ}$ ) and benzaldehyde.



*N:N'-Diphenyl-o-chlorobenzamidine*.—*o*-Chlorobenzanilide (m. p. 115°; 15 g.) and aniline (7 g.) were mixed and phosphorus oxychloride (100 c.c.) slowly added when a vigorous reaction occurred. It was heated in an oil-bath at 140°-150° for 5 hours, cooled, then slowly added to cold water (200 c.c.) and the solid obtained was collected. The solid was triturated with strong ammonium hydroxide and then this heated for half an hour. *N:N'-diphenyl-o-chlorobenzamidine* that separated was collected, washed and crystallised from alcohol as colorless needles, m. p. 130°, yield 15 g. (Found: Cl, 12.0.  $C_{19}H_{15}N_2Cl$  requires Cl, 11.5 per cent). It is soluble in EtOH, MeOH and acetone and less soluble in benzene and light petroleum.

The *hydrochloride* was obtained as prismatic needles, m. p. 297-98°. (Found: Cl, 20.8.  $C_{19}H_{15}N_2Cl \cdot HCl$  requires Cl, 20.7 per cent).

The *picrate* was prepared as shining yellow needles, m.p. 201-202°. (Found: Cl, 6.3.  $C_{25}H_{18}O_7N_5Cl$  requires Cl, 6.6 per cent).

*N.N'-Diphenyl-N-carbethoxy-o-chlorobenzamidine*.—To a solution of *N:N'*-diphenyl-*o*-chlorobenzamidine (15 g.) in dry benzene (200 c.c.) containing sodium bicarbonate (10.2 g.), ethyl chloroformate (4.8 g.) was slowly added with cooling in a freezing mixture. After keeping the reaction mixture overnight at 0°, it was filtered and benzene removed from the filtrate when a yellow paste was obtained. The paste after washing with light petroleum (60°-80°) was crystallised from dilute alcohol in shining white needles (8.0 g.), m. p. 169-70°. (Found: Cl, 9.6.  $C_{22}H_{19}O_2N_2Cl$  requires Cl, 9.4 per cent). The condensation was also carried out using ethyl acetate as a solvent with good results. It is sparingly soluble in petroleum, moderately in benzene and alcohol, and easily in chloroform.

The benzamidine (0.5 g.) when refluxed with alcoholic sodium hydroxide gave *N:N'*-diphenyl-*o*-chlorobenzamidine.

The benzamidine (0.5 g.) was heated with aniline (2 g.) at 180°-190° for 3½ hours when *sym*-diphenylurea, m. p. 242°, and *N:N'*-diphenyl-*o*-chlorobenzamidine, m. p. 130°, were formed.

*N:N'-Diphenyl-N-carbethoxydihydro-o-chlorobenzamidine*.—The above *N*-carbethoxybenzamidine (1.5 g.) in moist ethereal solution (200 c.c.) was added to aluminium amalgam (13 g.), and the reaction mixture was just warmed to start the reaction and kept aside. After about 20 minutes, it was filtered and the ether removed. The yellowish paste that remained was washed with light petroleum (20 c.c.) and crystallised from a mixture of light (b. p. 60°-80°) and heavy petroleum (b.p. 100°-120°) when *N.N'-diphenyl-N-carbethoxydihydro-o-chlorobenzamidine* separated in shining needles, m.p. 108-109°. (Found: Cl, 9.5.  $C_{22}H_{21}O_2N_2Cl$  requires Cl, 9.3 per cent). A good yield was obtained when reduction was carried out in moist ethyl acetate as a solvent.

The above dihydrobenzamidine (2 g.) was hydrolysed with concentrated hydrochloric acid when *o*-chlorobenzaldehyde, b.p. 210°-212° (0.4 g.) was obtained (Mayer and English, *Annalen*, 1918, 417, 78, give b.p. 213°-214°). 2:4-Dinitrophenylhydrazone, m.p. and mixed m.p. with one prepared from an authentic specimen of *o*-chlorobenzal-

dehyde, 211-12°. (Found: Cl, 11.5. Calc. for  $C_{13}H_9O_4N_4$ : Cl, 11.1 per cent). (Campbell, *Analyst*, 1936, **61**, 391, gives m.p. 206°).

*N:N'-Diphenyl-m-bromobenzamidine* was prepared as the corresponding *o*-chlorobenzamidine from *m*-bromobenzanilide (m.p. 148°; 35.0 g.), aniline (25.0 g.) and phosphorus oxychloride (200 c.c.) and crystallised from ethyl alcohol as tiny colorless needles (38.0 g.), m.p. 132°. (Found: Br, 22.8.  $C_{19}H_{13}N_2Br$  requires Br, 22.8 per cent). The *hydrochloride* was obtained as shining plates, m.p. 262°. (Found: hal., 29.6.  $C_{19}H_{13}N_2Br \cdot HCl$  requires hal., 29.8 per cent). The *picrate*, was obtained as yellow needles, m. p. 192°. (Found: Br, 13.4.  $C_{23}H_{16}O_7N_7Br$  requires Br, 13.7 per cent).

*N:N'-Diphenyl-N-carbethoxy-m-bromobenzamidine* was prepared from the above benzamidine (10.0 g.) by condensation with ethyl chloroformate (3.0 g.) in benzene solution in presence of sodium bicarbonate (8.0 g.) in prisms from a mixture of benzene and petroleum, m.p. 88-90°, yield 6.0 g. (Found: Br, 19.0.  $C_{22}H_{16}O_2N_2Br$  requires Br, 18.9 per cent).

*N:N'-Diphenyl-N-carbethoxydihydro-m-bromobenzamidine*.—The above *N*-carbethoxybenzamidine (2.0 g.) in moist ethereal solution was reduced with aluminium amalgam (20 g.) for 15 minutes at room temperature. The residue after washing with light petroleum (b.p. 60°-80°) was crystallised from a mixture of benzene and light petroleum in colorless glistening needles, m.p. 108°. (Found: Br, 18.8.  $C_{22}H_{21}O_2N_2Br$  requires Br, 18.8 per cent).

The dihydrobenzamidine (1.5 g.) was hydrolysed with concentrated hydrochloric acid to give *m*-bromobenzaldehyde (0.3 g.), b.p. 230°-233° (Mettler, *Ber.*, 1905, **38**, 2810, gives b.p. 228°-230°/726 mm.). 2:4-Dinitrophenylhydrazone was prepared as needles from ethyl acetate, m.p. 251-52°.

*N:N'-Diphenyl-p-bromobenzamidine* was prepared from *p*-bromobenzanilide (m. p. 198-99°; 20 g.), aniline (13 g.) and phosphorus oxychloride (80 c.c.) in needles from benzene and heavy petroleum (22 g.), m.p. 175°. The *hydrochloride* was prepared as prisms from glacial acetic acid, m.p. 292° (decomp.). (Found: hal., 30.1.  $C_{19}H_{15}N_2Br \cdot HCl$  requires hal., 30.1 per cent). The *picrate* was prepared in yellow needles from dilute alcohol, m.p. 194°. (Found: Br, 13.1.  $C_{23}H_{18}O_7N_7Br$  requires Br, 13.7 per cent).

*N:N'-Diphenyl-N-carbethoxy-p-bromobenzamidine* was prepared by the condensation of the above benzamidine (20 g.) with ethyl chloroformate (6 g.) in presence of sodium bicarbonate (10 g.) in benzene as prisms from a mixture of benzene and light petroleum, m.p. 107°, yield 11 g. (Found: Br, 18.8.  $C_{22}H_{19}O_2N_2Br$  requires Br, 18.9 per cent).

*Reduction of N:N'-Diphenyl-N-carbethoxy-p-bromobenzamidine*.—The reduction of the benzamidine (2 g.) was carried out with aluminium amalgam (20 g.) in moist ether (200 c.c.). As no solid dihydro product could be isolated from the product obtained on removal of ether, it was directly hydrolysed with concentrated hydrochloric acid when *p*-bromobenzaldehyde was obtained as needles, m.p. 56-57°, yield 0.3 g. (Adams and

Vollweiler, *J. Amer. Chem. Soc.*, 1918, **40**, 1738, give m.p. 56-57°. 2:4-Dinitrophenylhydrazone was obtained as red needles from ethyl acetate, m.p. 256-57°.

N:N'-Diphenyl-*o*-toluamidine was prepared from *o*-toluanilide (m.p. 130°; 30 g.), aniline (14.5 g.) and phosphorus oxychloride (120 g.) as long white needles from alcohol, m.p. 126-27°, yield 36 g. (Found: N, 9.7.  $C_{20}H_{18}N_2$  requires N, 9.8 per cent).

The *hydrochloride* was obtained as needles from ethyl alcohol, m. p. 290-92°. (Found: Cl, 11.1.  $C_{20}H_{18}N_2 \cdot HCl$  requires Cl, 11.0 per cent). The *picrate* was obtained as yellow prisms from methyl alcohol, m.p. 198°. (Found: N, 13.4.  $C_{26}H_{21}O_7N_5$  requires N, 13.6 per cent).

N:N'-Diphenyl-N-carbethoxy-*o*-toluamidine was prepared from the above *o*-toluamidine (10 g.), ethyl chloroformate (3 g.) and sodium bicarbonate (8 g.) in benzene as white prismatic needles from dilute methyl alcohol, m.p. 145°, yield 6 g. (Found: C, 76.8; H, 6.8; N, 8.1.  $C_{23}H_{22}O_2N_2$  requires C, 76.7; H, 6.1; N, 7.8 per cent).

*Reduction N:N'-Diphenyl-N-carbethoxy-*o*-toluamidine.*—The above N-carbethoxytoluamidine (2 g.) was reduced with aluminium amalgam (20 g.), the dihydro compound was not isolated but the reaction product was directly hydrolysed to *o*-tolualdehyde, b.p. 200° (Bornemann, *Ber.*, 1884, **17**, 1467, gives b.p. 199°-200°). 2:4-Dinitrophenylhydrazone, orange-red needles, m.p. 193-94° (Nauta, Ernstring and Faber, *Rec. trav. Chim.*, 1941, **60**, 915, m.p. 193-94°).

N:N'-Diphenyl-*m*-toluamidine was prepared from *m*-toluanilide (m.p. 133°; 15 g.), aniline (7 g.) and phosphorus oxychloride (45 c.c.) in tiny needles from dilute alcohol, m.p. 117°, yield 13.5 g. (Found: N, 10.0.  $C_{20}H_{18}N_2$  requires N, 9.8 per cent).

The *hydrochloride* was prepared as plates from alcohol, m. p. 265°. (Found: Cl, 10.9.  $C_{20}H_{18}N_2 \cdot HCl$  requires Cl, 11.0 per cent). The *picrate* as yellow needles from methyl alcohol, m.p. 190°. (Found: N, 13.5.  $C_{26}H_{21}O_7N_5$  requires N, 13.6 per cent).

N:N'-Diphenyl N-carbethoxy-*m*-toluamidine was obtained when the above toluamidine (10 g.) was condensed with ethyl chloroformate (3 g.) in presence of sodium bicarbonate (8 g.) in benzene, as prisms from alcohol, m.p. 86°, yield 5.5 g. (Found: C, 76.0; H, 5.4; N, 8.0.  $C_{23}H_{22}O_2N_2$  requires C, 76.7; H, 6.1; N, 7.8 per cent).

*Reduction of N:N'-Diphenyl-N-carbethoxy-*m*-toluamidine.*—The above N-carbethoxytoluamidine (2 g.) was reduced with aluminium amalgam (20 g.) and the reduction product without isolation was hydrolysed to *m*-tolualdehyde, b.p. 201° (Gundeloh, *Bull. soc. chim.*, 1876, ii, **26**, 44, b.p. 199°).

The 2:4-dinitrophenylhydrazone was obtained as orange needles, m. p. 207°. (Found: N, 18.4.  $C_{14}H_{12}O_4N_4$  requires N, 18.7 per cent).

N:N'-Diphenyl-*p*-toluamidine was prepared from *p*-toluanilide (m.p. 147°; 30 g.), aniline (14 g.) and phosphorus oxychloride (120 g.) as needles from alcohol, m.p. 170°, yield 35 g. (Found: N, 9.7. Calc. for  $C_{20}H_{18}N_2$ : N, 9.8 per cent) (Glock, *Ber.*, 1898, **21**, 2665, m.p. 168°). The *hydrochloride* was obtained as plates from acetic acid, m.p.

272° (Found: Cl, 10.8.  $C_{10}H_{11}N_2.HCl$  requires Cl, 11.0 per cent) and the *picrate*, as yellow needles from dilute alcohol, m.p. 210° (Found: N, 13.6.  $C_{26}H_{21}O_7N_3$  requires N, 13.6 per cent).

*N:N'-Diphenyl-N-carbethoxy-p-toluamide* was prepared from the above toluamide (15 g.), ethyl chloroformate (5.6 g.) and sodium bicarbonate (12 g.) and crystallised from alcohol as colorless prismatic needles, m.p. 115-16°, yield 6.0 g. (Found: C, 77.0; H, 5.1; N, 8.0.  $C_{23}H_{21}O_2N_2$  requires C, 76.7; H, 6.1; N, 7.8 per cent).

*N.N'-Diphenyl-N-carbethoxydihydro-p-toluamide* was obtained when the above *N-carbethoxytoluamide* (1.0 g.) was reduced with aluminium amalgam (8 g.) as white shining needles from petroleum and benzene mixture, m.p. 114-15°, yield 0.8 g. (Found: N, 7.5.  $C_{23}H_{24}O_2N_2$  requires N, 7.8 per cent).

It was hydrolysed with concentrated hydrochloric acid when *p*-tolualdehyde, b.p. 204°-208° was obtained (Bornemann, *loc. cit.*, b.p. 204-205°). 2:4-Dinitrophenylhydrazone was obtained as red needles from ethyl acetate, m.p. and mixed m.p., 230° (Nauta, Ernsting and Faber, *loc. cit.*, m.p. 235°).

ORGANIC CHEMISTRY LABORATORIES,  
ROYAL INSTITUTE OF SCIENCE,  
BOMBAY.

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## QUINOLINE COMPLEXES OF ZINC AND CADMIUM SULPHATES AND THEIR HEATS OF FORMATION

BY G. C. BHATTACHARYA AND P. C. SINHA

Quinoline complexes of zinc sulphate and cadmium sulphate have been prepared. They have the formulae  $[Zn.2C_9H_7N]SO_4.8H_2O$  and  $[Cd.2C_9H_7N.2H_2O]SO_4.4H_2O$  respectively. The heats of formation of these compounds have been determined calorimetrically by the method of solution. The heats of formation of the zinc and cadmium compounds are 15,704 and 17,206 calories/G. F. W respectively. It appears that the introduction of water molecules inside the complex increases its stability.

A large number of complexes of quinoline with various inorganic salts is known, but no attempt has yet been made to make a systematic study of these complexes. All the earlier works are concerned mainly with the preparation and analysis of the complex formed, and except the solubility, decomposition temperature and a few crystallographic data, little regarding the physical properties of these complexes is recorded in literature. Heat data, which are of importance in determining their stability, in obtaining a comparative picture of the complexes of different organic heterocyclic bases with inorganic salt, and in arriving at any kind of generalisation, are not available. In the present investigation the quinoline complexes of the sulphates of zinc and cadmium have been prepared and their heats of formation determined directly by calorimetric measurements. The sulphates of zinc and cadmium have been chosen because no quinoline complexes of these salts are known.

The quinoline complexes of zinc and cadmium were first prepared by Schiff (*Compt. rend.*, 1863, **57**, 838; *Annalen*, 1864, **131**, 112). He obtained the quinoline complexes of the chlorides and iodides of zinc and cadmium and established their compositions as  $ZnCl_2.2Q$ ,  $ZnI_2.2Q$ ,  $CdCl_2.2Q$  and  $CdI_2.2Q$ , by analysis. Borsbach (*Ber.*, 1890, **23**, 435) also obtained the same compounds and found that they were only slightly soluble in water and alcohol. He also prepared the complexes,  $CdCl_2.Q$  and  $CdBr_2.Q$  and also complexes of the type  $CdCl_2.Q.HCl.H_2O$ . Reitzenstein (*Z. anorg. Chem.*, 1898, **18**, 295) confirmed the formation of the complex  $CdBr_2.2Q$ . Hugo (*Chem. Zentr.*, 1905, **II**, 139) has given the crystallographic data of zinc and cadmium quinoline complexes of the type  $Zn(NCS)_2.2C_9H_7N.NCS$ ,  $ZnCl_2.2C_9H_7N.Cl$ ,  $ZnBr_2.2C_9H_7N.Br$ ,  $ZnI_2.2C_9H_7N.I$  and  $CdBr_2.2C_9H_7N.Br$ . No quinoline complex of either zinc sulphate or cadmium sulphate was known. More recently, Chang and Yu (*Z. anorg. Chem.*, 1939, **243**, 14) studied the complexes of quinoline with some bivalent heavy metals. They prepared the compounds,  $2CuSO_4.5C_9H_7N$ ,  $2CuSO_4.C_9H_7N$ ,  $2CoSO_4.C_9H_7N$  and  $2HgSO_4.C_9H_7N$ . As a result of their investigation they came to the conclusion that the presence of a multivalent anion decreases the tendency of the bivalent metals to form complexes with quinoline. The present work, however, does not support their observation.

### EXPERIMENTAL

Freshly distilled quinoline (20 c.c.) was taken in a tall beaker and a saturated solution of zinc sulphate or cadmium sulphate was added to it dropwise from a burette

until no further crystals separated. The liquid was kept vigorously agitated by means of an electrically operated stirrer. The stirring was continued for several hours even after the addition of the sulphate solution had been completed. The crystals were collected on a Buchner funnel, washed with a little acetone, dried between folds of filter paper and preserved.

The analysis of the compounds thus obtained was carried out as follows: Quinoline was determined by weighing out a small quantity of the substance into an Erlenmeyer's flask, treating with an excess of *N*/10-hydrochloric acid and titrating back the excess of acid with standard NaOH solution, using methyl orange as an indicator. Zinc was estimated by precipitating as zinc ammonium phosphate and weighing as zinc pyrophosphate. Cadmium was determined as the sulphide and the sulphate ion was estimated in the usual way by precipitating with barium chloride. The results of analysis are set down in Table I.

TABLE I

Complex.	Found.	Calc.
$\text{ZnSO}_4 \cdot 2\text{Q} \cdot 8\text{H}_2\text{O}$	Zn, 11.5, 11.4, 11.2%	11.6%
	Q, 46.0, 45.9, 45.6	45.8
	$\text{SO}_4$ , 17.6, 17.4, 17.2	17.4
	$\text{H}_2\text{O}$ , —	25.2
$\text{CdSO}_4 \cdot 2\text{Q} \cdot 6\text{H}_2\text{O}$	Cd, 20.0, 19.8, 19.4%	19.6
	Q, 45.2, 44.8, 44.2	44.9
	$\text{SO}_4$ , 17.1, 16.8, 16.6	16.7
	$\text{H}_2\text{O}$ , —	18.8

Both the compounds are colorless and crystalline. They are not hygroscopic, and both are decomposed by water, the zinc complex being more so. They are readily soluble in mineral acids, but are insoluble in acetone, alcohol and chloroform. When the hydrated compounds were kept over concentrated sulphuric acid in a vacuum desiccator at 30°, it was found that the zinc compound lost all the water in one week and the anhydrous complex,  $\text{ZnSO}_4 \cdot 2\text{C}_9\text{H}_7\text{N}$ , was left. Under the same conditions the cadmium compound, however, lost only 4 molecules of water and the remaining two molecules of water were retained permanently. There was no loss even after the crystals were left in the desiccator for over a month.

The heats of formation of the complexes were determined by solution methods. The heat of solution of the complex in 2*N*-sulphuric acid was first determined and then the heat of solution of quinoline in sulphuric acid of the same strength was measured similarly. Knowing the heat of solution of pure zinc sulphate or cadmium sulphate (cf. International Critical Tables), it is possible to calculate the heats of formation of the complexes from the results obtained. The method of calorimetry was similar to that used by Patrick and Grimm (*J. Amer. Chem. Soc.*, 1921, **43**, 2144). The calorimeter

consisted of a silvered Dewar flask of 100 c. c. capacity. It was fitted with a rubber cover in which were mounted a 5° Beckmann thermometer, a Nichrome-wire heater, and a copper stirrup which served as a stirrer as well as a holder for the glass bulbs in which a weighed quantity of the complex or quinoline had been sealed. The glass bulbs were broken beneath the surface of the liquid by means of a rod. The vacuum flask contained a charge of only 25 c. c. of 2*N*-sulphuric acid and it was found that intermittent manual stirring was sufficient to keep the temperature equalised. Repeated calibration using a measured heat input through the Nichrome coil showed that the reproducibility of the measurements was quite good. To prevent the action of acid, etc., the Nichrome wire was wound round a thin strip of mica and immersed in oil contained in a thin-walled glass tube, similar to the one used by Tucker (*Trans. Roy. Soc.*, 1915, 215, 319) in his heat of dilution experiments. The results of measurements are recorded in Table II.

TABLE II

Substance	Weight.	Temp rise (corr. °C).	Thermal capacity of calori- meter.	Heat of solution, G.F.W.	Mean
$\text{ZnSO}_4 \cdot 2\text{C}_9\text{H}_7\text{N} \cdot 8\text{H}_2\text{O}$	(1) 1.4882 g.	0.702°	58.2	15,440	$Q_1$ 15,286
	(2) 1.5500	0.704°	58.4	14,940	
	(3) 1.5723	0.742°	58.3	15,480	
Quinoline	(1) 1.3333	1.112°	58.2	6,252	$Q_2$ 6,280
	(2) 0.9430	0.800°	58.0	6,348	
	(3) 0.6149	0.512°	58.1	6,241	
$\text{CdSO}_4 \cdot 2\text{C}_9\text{H}_7\text{N} \cdot 6\text{H}_2\text{O}$	(1) 1.0984	0.202°	58.1	6,138	$Q_1$ 6,094
	(2) 1.2238	0.225°	58.2	6,116	
	(3) 1.3101	0.242°	58.0	6,030	
$\text{ZnSO}_4$				18,430	$Q_3$ International Critical Table
$\text{CdSO}_4$				10,740	

If the heat of solution of complex is  $Q_1$  and those of quinoline and  $\text{ZnSO}_4$  or  $\text{CdSO}_4$  are  $Q_2$  and  $Q_3$  respectively, then the heat of formation of the complex, according to Hess' law, is  $Q_3 + 2Q_2 - Q_1$ . Heats formation of the two complexes,  $\text{ZnSO}_4 \cdot 2\text{C}_9\text{H}_7\text{N} \cdot 8\text{H}_2\text{O}$  and  $\text{CdSO}_4 \cdot 2\text{C}_9\text{H}_7\text{N} \cdot 6\text{H}_2\text{O}$  work out to 15,704 calories/G. F. W and 17,206 calories/G. F. W. respectively. The effect of a small amount of water present in the crystals of the complexes being extremely small is neglected in the calculations.

## DISCUSSION

The facts that the whole of the water in the zinc complex is readily removable and the sulphate ion is capable of complete ionisation indicate that the formula of the

zinc compound is  $[\text{Zn} \cdot 2\text{C}_9\text{H}_7\text{N}]\text{SO}_4 \cdot 8\text{H}_2\text{O}$ . In the case of the cadmium compound, however, only 4 molecules of water can be removed by dehydration, but 2 molecules of water are permanently retained, indicating that these 2 molecules of water form part of the complex itself. Hence the formula of this compound seems to be  $[\text{Cd} \cdot 2\text{C}_9\text{H}_7\text{N} \cdot 2\text{H}_2\text{O}]\text{SO}_4 \cdot 4\text{H}_2\text{O}$ .

It has been found that heat of formation of  $[\text{Zn} \cdot 2\text{C}_9\text{H}_7\text{N}]\text{SO}_4 \cdot 8\text{H}_2\text{O}$  is 15,602 calories/G F.W. and that  $[\text{Cd} \cdot 2\text{C}_9\text{H}_7\text{N} \cdot 2\text{H}_2\text{O}]\text{SO}_4 \cdot 4\text{H}_2\text{O}$  is 17,198 calories/G. F. W. showing that the cadmium compound is more stable than the zinc compound. It is probable that the introduction of two  $\text{H}_2\text{O}$  molecules in the complex increases the stability of the compound. The heats of formation are comparable in magnitude with those of similar complexes of pyridine.

The work of Schiff, Borsbach, and Reitzenstein (*loc cit.*) shows that the chlorides, bromides and iodides of zinc and cadmium form, with quinoline, complexes almost identical in composition with the sulphates of these metals. The stability of the quinoline complexes of zinc and cadmium salts appears to be of the same order whether the anions are univalent or bivalent. The present work therefore does not support the conclusion of Chang and Yü (*loc. cit.*) that the presence of a multivalent anion decreases the tendency of the bivalent metals to form complexes with quinoline.

The authors' thanks are due to Dr R. C. Ray for his keen interest in the work.

CHEMICAL LABORATORY,  
SCIENCE COLLEGE, PATNA.

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## ESSENTIAL OIL FROM THE LEAVES OF *BLUMEA LACERA*

By K. K. BASLAS AND S. S. DESHAPANDE

The essential oil from the leaves of '*Blumea lacera*' consists of 66% cineol, 10% *d*-fenchone and about 6% citral

The plant '*Blumea lacera*' known in Hindi as "Kakronda" and in Sanskrit as "Kukradru" is indigenous to India. It grows in fields near Agra and generally throughout North India. It is a small bushy plant with wooly leaves and belongs to the family of Compositae. It is regarded as highly medicinal and is specially used to cure skin diseases.

Another species, *Blumea balsamifera*, has been worked out by Jonas (*Schimmel's Ber.*, 1909, April, p. 152) who mentions the cineol, limonene, *l*-borneol, *l*-camphor etc. as the chief components of its essential oil.

As will be seen from the following, the composition of the oil extracted by us from *Blumea lacera* is different.

The essential oil was obtained by steam distillation of its leaves in 0.5% yield. It is a greenish yellow oil with following properties:—  $d_{20}^4$ , 0.982;  $n_D^{20}$ , 1.490;  $[\alpha]_D^{20}$ , 31.6°.

The oil (60 c.c.) was distilled at reduced pressure (30 mm.) and the following fractions were collected:—

(I) 78°-80°, 40 c.c. (II) 80°-120°, 10 c.c. (III) 120°-135°, 6 c.c.

Fraction (I) was strongly odorous. At atmospheric pressure it distilled almost wholly at 178°. It absorbed bromine but gave no nitrosite or nitrosyl chloride. It did not reduce Fehling's solution or ammoniacal silver nitrate and did not form any semicarbazone. As its odour resembled that of eucalyptus oil the presence of cineol was suspected and was confirmed on examination. Thus the fraction formed a solid additive compound with syrupy phosphoric acid (cf. Kebler, *Amer. J. Pharm.*, 1898, 70, 492). It also forms a crystalline compound with resorcinol melting at 85-87° and on two crystallisations at 87-90° (Baeyer and Virck, *Ber.*, 1902, 35, 1209, mention m.p. 80-85°). On warming this product with aqueous caustic soda the regenerated cineol, obtained by extraction, boiled at 178°. Identity of this fraction with cineol was finally confirmed by comparing the above tests with genuine sample of cineol obtained from eucalyptus oil. The percentage of cineol in the oil calculated from the weight of the fraction is 66.

Fraction (II) (10 c.c.) was redistilled at 30 mm. pressure when 6 c.c. passed at 91° and the remaining 4 c.c. of the contents distilled within a wide range of 92°-120°. The portion passing at 91° appeared to be a distinct individual and when it was distilled at atmospheric pressure it boiled at 192°. Analysis of this fraction corresponds with the composition  $C_{10}H_{16}O$ .

The component  $C_{10}H_{16}O$  does not reduce Fehling's solution or ammoniacal silver nitrate and also does not form any solid derivative characteristic of hydroxyl group. It, however, forms an oxime, m.p.  $163^{\circ}$  and a semicarbazone, melting at  $184^{\circ}$  and on recrystallisation at  $186-87^{\circ}$ . The composition of the semicarbazone determined by analysis corresponds with the semicarbazone of the ketone,  $C_{10}H_{18}O$ .

From the boiling point and results of analysis of the ketone and from the melting point of its oxime and that of its semicarbazone the ketone is identified as *d*-fenchone (b.p.  $192^{\circ}-194^{\circ}$ ; oxime, m.p.  $163^{\circ}$ ; Mahla and Tiemann, *Ber.*, 1896, **29**, 2818); semicarbazone, m.p.  $186-87^{\circ}$  (Rimini, *Gazzetta*, 1900, **30**, 600). Calculated from the amount of this fraction the ketone forms 10% of the total oil.

Fraction (III) boiling between  $120^{\circ}$  and  $135^{\circ}/30$  mm. proved to be unstable and could not be distilled at atmospheric pressure without polymerisation. However, on rapid distillation a small amount distilled at  $230^{\circ}$ . It proved to be an aldehyde as it reduced Fehling's solution and formed a sodium bisulphite compound. From its boiling point and the ease with which it polymerised it was suspected to be citral. The bisulphite compound was more easily prepared by Tiemann's method (*Ber.*, 1898, **31**, 3311) and the method suggested by Tiemann for preparing semicarbazone from bisulphite compound in the case of citronellal (*ibid.*, p. 3307) was used in the present case with the modification that free acetic acid was used. This gave a semicarbazone melting at  $163^{\circ}$  (semicarbazone of citral- $\alpha$  melts at  $163^{\circ}$ ). The identity of citral in fraction (III) was confirmed by comparing the results of these tests with a genuine sample of citral obtained from lemon grass oil. From the weight of the fraction the percentage of citral in the oil is about 6.

TABLE I

Fraction No	B.p. (30 mm.)	Vol.	Yield.	Properties	
				B p. at atmospheric pressure	M p. of derivatives
I	$78^{\circ}-80^{\circ}$	40 c.c.	66%	$178^{\circ}$	Compound with resorcinol ( $87^{\circ}-90^{\circ}$ )
II	$80^{\circ}-120^{\circ}$	10 ↓ Refractionated ↓	• •		
(a)	$91^{\circ}$	6 c.c.	10%	$192^{\circ}$	Oxime (m.p. $163^{\circ}$ ) Semicarbazone m.p. $186-87^{\circ}$
(b)	$92^{\circ}-120^{\circ}$	3	—	—	—
III	$120^{\circ}-135^{\circ}$	6	6	About $230^{\circ}$ with polymerisation	Semicarbazone, m.p. $163^{\circ}$

## E X P E R I M E N T A L

*Isolation of the Oil.*—The essential oil was obtained by steam distillation of the leaves from a copper still fitted with a spiral copper condenser. The steam distillate was extracted with carbon tetrachloride, the extract dried and the solvent removed on a water-bath. The greenish yellow oil obtained in 0.5% yield has the properties given in the introductory part.

*Fractionation of the Oil.*—The fractions obtained by distilling 60 c.c. of the oil at 30 mm. pressure, their boiling ranges, percentage yield and properties are given in Table I.

*Identification of Cineol in Fraction (I): Cineol-phosphoric acid Addition Compound.*—To the fraction (2.5 c.c.), cooled by ice and salt, was added dropwise 1 c.c. of syrupy phosphoric acid ( $d\ 1.75$ ), similarly cooled. Thorough mixing is necessary. The addition product immediately separated as a pasty solid which became harder on further cooling.

*Cineol-resorcinol Addition Compound.*—Resorcinol (0.5 g.) was added to 2.5 c.c. of the fraction and the mixture warmed until resorcinol went into solution. On cooling, the addition product separated in rhombic plates. On filtering, washing with a little alcohol and drying the compound melted at  $85-87^{\circ}$ . Two crystallisations from alcohol raised the melting point of the product to  $87-90^{\circ}$ .

*Identification of d-Fenchone in Fraction (II).*—The fraction boiling at  $91^{\circ}/30$  mm. or at  $192^{\circ}$  at atmospheric pressure was analysed: (Found: C, 79.2; H, 10.2.  $C_{10}H_{16}O$  requires C, 78.9; H, 10.5 per cent).

*Oxime of d-Fenchone.*—To alcoholic solution of this fraction was added aqueous solution of hydroxylamine hydrochloride, neutralised with equivalent amount of caustic potash. After filtering off the potassium chloride and refluxing on a water-bath for 2 to 3 hours the solution was poured on a watch glass. The oxime which separated was freed from adhering liquid and on crystallisation from alcohol and ethyl acetate it melted at  $163^{\circ}$ .

*Semicarbazone of d-Fenchone.*—On adding the fraction to an aqueous concentrated solution of semicarbazide hydrochloride and sodium acetate and on occasional shaking the semicarbazone began to separate after two days and on standing for one week the separation was complete. On crystallising from dilute alcohol it melted at  $184^{\circ}$ . Further crystallisation, twice from the same solvent, raised the melting point to  $186-87^{\circ}$ . (Found: C, 63.1; H, 10.9; N, 19.6.  $C_{11}H_{16}ON$ , requires C, 63.1; H, 9.0; N, 20.0 per cent).

*Sodium Bisulphite Compound and Semicarbazone of Citral in Fraction (III).*—A cold saturated solution of sodium sulphite was added to this fraction kept cool by ice. On

gradually adding acetic acid and vigorous shaking crystals of the bisulphite compound began to separate. These were filtered, freed from adhering oil and dissolved in excess of water. On adding a concentrated solution of semicarbazide hydrochloride, sodium acetate and free acetic acid and on cooling thoroughly, the semicarbazone began to separate, which on crystallisation from dilute alcohol melted at  $163^{\circ}$ .

CHEMICAL LABORATORY,  
AGRA COLLEGE, AGRA.

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## DISSOCIATION PRESSURES AND PRESSURE-COMPOSITION ISOTHERMALS OF COPPER PYRIDINE NITRATES

By N. G. MITRA AND P. C. SINHA

The dissociation pressures of the pyridine complexes of copper nitrate have been measured at different temperatures and the isothermal curves showing pressures against number of molecules of pyridine per molecule of copper nitrate have been determined at 30°. From these results it has been proved that in the solid phase three complexes, namely  $\text{Cu}(\text{NO}_3)_2 \cdot 6 \text{ py}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 5 \text{ py}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 4 \text{ py}$  are formed. The heats of dissociation of the three complexes have been calculated by the help of Clapeyron-Clausius equation and the linear graphs  $-\log_{10} p$  against  $10^6/T$ ; and their values correspond to 8,950 cal, 13,420 cal and 14,350 cal respectively showing that the 4-pyridine complex is the most stable and the 6-pyridine complex, the least so.

By measurement of dissociation pressures of copper pyridine perchlorates at different temperatures and study of pressure-composition isothermals of copper perchlorate-pyridine system at 30° and 50°, Sinha and Ray (*Trans. Faraday Soc.*, 1948, **44**, 790) have proved that in the solid phase only two stable complexes, viz.,  $\text{Cu}(\text{ClO}_4)_2 \cdot 6 \text{ py}$  and  $\text{Cu}(\text{ClO}_4)_2 \cdot 4 \text{ py}$  are formed. From determination of the partition coefficient of copper perchlorate between water and pyridine, the same authors (*this Journal*, 1948, **26**, 247) have shown that the two complexes  $\text{Cu}(\text{ClO}_4)_2 \cdot 4 \text{ py}$  and  $\text{Cu}(\text{ClO}_4)_2 \cdot 6 \text{ py}$  are present in aqueous solutions. The present investigation was undertaken with a view to ascertaining the influence, if any, of the anion on the composition and stability of the complexes formed under similar conditions. The nitrate ion being much smaller in size than the perchlorate ion was therefore selected for the study. The dissociation pressures of copper pyridine nitrates have been measured at different temperatures, and the number of copper pyridine nitrates, which are definitely formed under laboratory conditions, has also been determined by an isothermal study of the copper nitrate-pyridine system at 30°. In the present case indication of the formation of four complexes has been obtained. The complex which contains the highest amount of pyridine approximates to  $\text{Cu}(\text{NO}_3)_2 \cdot 7 \text{ C}_5\text{H}_5\text{N}$ , but as the dissociation pressures of this complex with temperature are not reproducible, it appears that it is not a stable compound, but it is formed by adsorption, and is therefore left out. The other three complexes, namely,  $\text{Cu}(\text{NO}_3)_2 \cdot 6 \text{ py}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 5 \text{ py}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 4 \text{ py}$ , which give reversible and reproducible dissociation pressures, must be regarded as definite compounds. It will be noticed that the complexes of pyridine obtained with copper nitrate are similar to those which are formed with copper perchlorate, indicating that the anion has little or no influence in determining the nature and composition of the complexes formed.

### EXPERIMENTAL

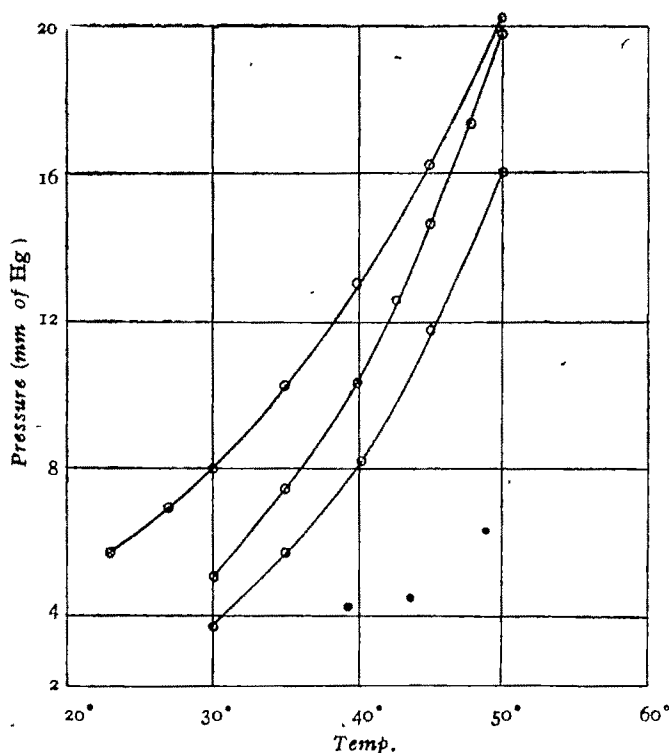
Copper nitrate-pyridine complex was prepared by the method of Grossmann (*Per.*, 1904, **37**, 1254) by treating a cold saturated solution of copper nitrate with excess of

pyridine, filtering the precipitated substance on a Buchner funnel and washing with pyridine.

The apparatus used for the determination of the dissociation pressures and the procedure followed have been described in a previous paper by Sinha and Ray (*Trans. Faraday Soc.*, 1948, **44**, 790). The experiments were carried out in an air-thermostat, the temperature of which was controlled electrically and maintained constant to  $\pm 0.1^\circ$ . The substance was placed in a bulb which was sealed to a closed limbed manometer. The thermostat was set to different temperatures and the pressures determined by reading the heights of mercury in the two limbs of the manometer by means of a cathetometer.

The results obtained are recorded in Table I and represented graphically in Fig. 1. The logarithms of pressures are also plotted against the reciprocals of the absolute temperature and the linear graphs thus obtained are shown in Fig. 2.

FIG. 1



The determination of isothermals consisted mainly of the measurements of the loss of weight of pyridine with its gradual removal at a fixed temperature. The loss of weight of the bulb containing the complex with progressive removal of pyridine was determined by weighing the bulb at intervals and the corresponding dissociation pressures were also measured. Thus a series of pressure values and the weights corresponding to each pressure were obtained. The apparatus used and the method of working

have been fully described in a previous paper (Sinha and Ray, *loc. cit.*). The results obtained are recorded in Table II and shown in Fig. 3 where the pressures are plotted against the number of molecules of pyridine per molecule of copper nitrate. The isothermals were determined at 35°. The determinations could not be made at higher temperatures because the compound began to decompose at 50°.

TABLE I

*Temperature-pressure values.*

System $\text{Cu}(\text{NO}_3)_2 \cdot 6/5 \text{ py.}$				System $\text{Cu}(\text{NO}_3)_2 \cdot 5/4 \text{ py.}$				System $\text{Cu}(\text{NO}_3)_2 \cdot 4/0 \text{ py}$			
Temp (t°)	Pressure (mm. Hg)	$\log_{10} p$	$1/T \times 10^6$	Temp (t°)	Pressure (mm. Hg)	$\log_{10} p$	$1/T \times 10^6$	Temp. (t°)	Pressure (mm. Hg.)	$\log_{10} p$	$1/T \times 10^6$
23	5.7	0.7559	3378	30	5.0	0.6990	3300	30	3.7	0.5682	3300
27	6.9	0.8423	3333	35	7.4	0.8692	3247	35	5.6	0.7482	3247
30	8.0	0.9031	3300	40	10.3	1.0128	3195	40.1	8.1	0.9085	3194
35	10.2	1.0102	3247	45	14.6	1.1644	3145	45	11.7	1.0682	3145
40	13.0	1.1139	3195	50	19.8	1.2967	3096	50	16.0	1.2041	3096
45	16.2	1.2101	3145								
50	20.2	1.3054	3096								

Mean value of the heat of dissociation (calc. from the graph),  
8,950 cal.

Mean value of the heat of dissociation (calc. from the graph),  
13,420 cal.

Mean value of the heat of dissociation (calc. from the graph),  
14,350 cal.

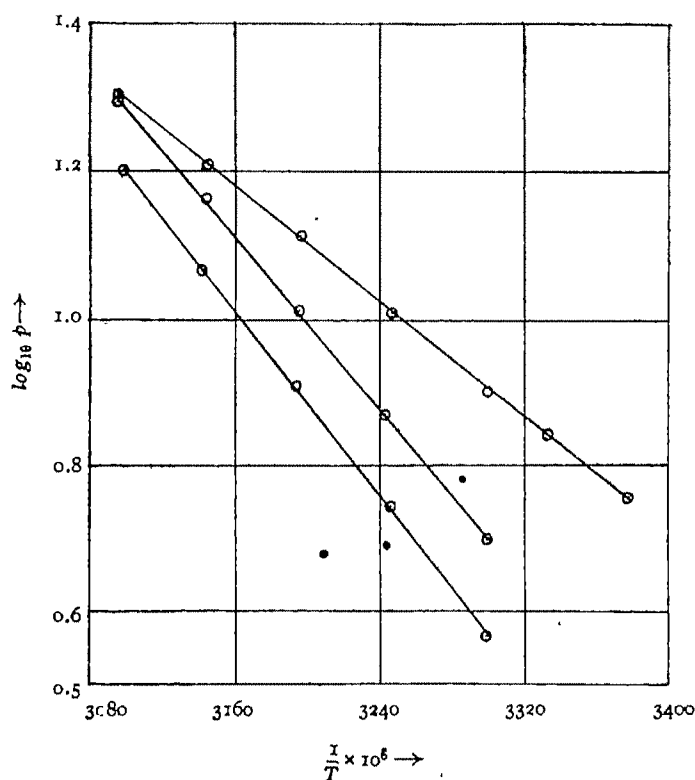
TABLE II

Pressure.	Loss in wt. of the bulb.	Loss in number of mols. of py per mol. of $\text{Cu}(\text{NO}_3)_2$ .	No. of mols. of py in the bulb per mol. of $\text{Cu}(\text{NO}_3)_2$ .	Pressure.	Loss in wt. of the bulb.	Loss in number of mols. of py per mol. of $\text{Cu}(\text{NO}_3)_2$ .	No. of mols. of py in the bulb per mol. of $\text{Cu}(\text{NO}_3)_2$ .
27 mm.	...	...	8.960	8 mm.	0.0280	0.205	4.314
"	0.1450 g.	1.059	7.900	"	0.0260	0.190	4.124
"	0.2400	1.754	6.14	"	0.0086	0.063	4.061
"	0.0158	0.115	6.032	3.7	0.0157	0.115	3.946
8 mm.	0.0176	0.129	5.903	"	0.0184	0.135	3.811
"	0.0131	0.096	5.807	"	0.0581	0.425	3.385
"	0.0143	0.105	5.702	"	0.0373	0.275	3.111
"	0.0132	0.096	5.606	"	0.0412	0.301	2.810
"	0.0159	0.116	5.490	"	0.0567	0.414	2.396
"	0.0201	0.147	5.343	"	0.0471	0.343	2.053
"	0.0430	0.314	5.029	"	0.0398	0.291	1.762
"	0.0480	0.351	4.678	"	0.0467	0.341	1.421
"	2.0218	0.159	4.519				

## DISCUSSION

The results of measurements of the dissociation pressures at varying temperatures and the determination of pyridine molecules per molecule of copper nitrate isothermally at  $30^\circ$  leave no doubt that three stable complexes are formed, namely,  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{py}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{py}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{py}$ . It must be mentioned, however, that vapour pressure measurements gave indication of the formation of a complex containing more than six molecules of pyridine attached to a molecule of copper nitrate. As these pressure values were not always reproducible, and especially as no break corresponding to this complex could be obtained in the isothermal studies, they were left out. It appears that loose adsorption compounds are formed. When the dissociating complex is in contact with an arbitrarily fixed concentration of pyridine vapour, it may be assumed that this is in equilibrium with the adsorbed pyridine molecules on the surface of finely divided and porous solid product and this equilibrium extends also to the reaction interface. A similar phenomenon was observed by Topley and Smith (*J. Chem. Soc.*, 1935, 321) in their study of the kinetics of salt hydrate dissociation:  $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \text{MnC}_2\text{O}_4 + 2\text{H}_2\text{O}$ .

FIG. 2



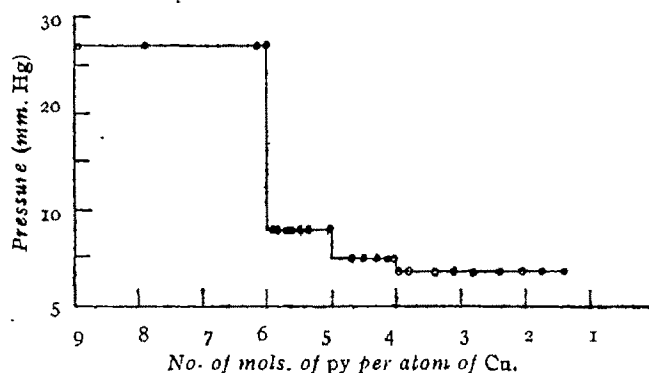
The graphs obtained by plotting  $\log_{10} p$  against  $(1/T) \times 10^5$  are straight lines as shown in Fig. 2. The heats of formation of the three pyridine complexes can be calculated by the help of Clapeyron—Clausius equation and the slope of the linear



graphs of  $\log_{10} p$  against  $(1/T)$ . The mean values of the heats of formation of the three complexes,  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{py}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{py}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{py}$ , are thus found to be 8,950 cals., 13,420 cals. and 14,350 cals. respectively, showing that the 4-pyridine complex is the most stable and the 6-pyridine complex, the least so, while the stability of the 5-pyridine complex is intermediate between these two.

Dissociation pressures have been measured up to  $50^\circ$ . The measurements could not be carried out at higher temperatures on account of the oxidising action of the nitrate ions on pyridine with consequent decomposition of the compounds, and for this reason isothermal measurements could not be made at  $50^\circ$  or at higher temperatures. It has therefore not been possible to determine the transition temperatures of the complexes.

FIG. 3



It will be seen (Fig. 3) that the isothermal study shows three definite breaks corresponding to the three complexes,  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{py}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{py}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{py}$ . In a previous paper Sinha and Ray (*loc. cit.*) showed that in the solid phase copper perchlorate formed with pyridine two stable complexes, namely  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{py}$  and  $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{py}$  under similar conditions. It will thus be seen that the limits of the pyridine molecules which can combine with the copper salts are the same in the two cases, indicating that the nature and the size of the anion have little or no influence in the formation of the complexes.

CHEMICAL LABORATORY,  
SCIENCE COLLEGE, PATNA.

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## POSSIBILITY OF SEPARATION OF COPPER AND SILVER ZONES IN AN ALLOY OF COPPER AND SILVER BY ZINC, CHROMATOGRAPHICALLY

By B. S. SRIKANTAN AND V. KRISHNAN

It is found that the chromatographic order Cu-Ag-Zn with alumina as adsorbent is reversed in dilute solutions to Cu-Zn-Ag. This is shown to be due to the preferential adsorption of  $Zn^{++}$  over the  $Ag^+$  in dilute solutions. It is suggested that this method may be used to separate and estimate the Cu-Ag alloys

Schwab and Jokers (*Z. angew. Chem.*, 1937, 50, 546) describe  $Cu^{++}$ - $Ag^+$ - $Zn^{++}$  as the order of chromatographic adsorption from top to bottom in a column of alumina, from solutions of mixed ions. With the developer ammonium sulphide, copper gives a dark colour and silver, a dark grey zone. Estimation of copper-silver alloys is not good by this process since the two zones are not well marked. It is necessary to separate the two zones by interposition with another of different colour, possibly white. During

FIG. 1



I—Chromatogram Cu-Ag-Zn (black-dark grey-white)  
II— „ Cu-Zn-Ag (black-white-dark grey)  
Developer— $(NH_4)_2S$  saturated with  $H_2S$

our experiments on the estimation of brass by chromatographic method (this *Journal*, 1949, 26, 415) attempts were made to separate the copper and zinc zones by the interposition of different ions. While confirming the work of these authors it was found that the chromatographic order was sometimes reversed and we obtained  $\text{Cu}^{++}$  -  $\text{Zn}^{++}$  -  $\text{Ag}^+$  as the order of separation. The chromatogram Cu-Zn-Ag (black-white-grey), developed by ammonium sulphide, saturated with hydrogen sulphide, was uniform and the lines of separation were quite sharp and horizontal. The previous authors worked with solutions of  $M$  and  $M/10$  only. In our experiments the concentrations of solutions were from  $N/25$  to  $N/200$ . This reversal is perhaps due to the preferential adsorption of the  $\text{Zn}^{++}$  ions over that of  $\text{Ag}^+$  ions at lower concentrations. Experiments were therefore undertaken on the adsorption of silver and zinc ions from their respective salt solutions at different concentrations.

The methods of setting up of the column and working are exactly the same as in the previous paper. Fig. 1 shows the chromatograms mentioned in this paper.

#### EXPERIMENTAL

*Adsorption of  $\text{Ag}^+$  and  $\text{Zn}^{++}$  on Alumina: Silver Nitrate.*—Alumina (3 g.), described in the previous paper, was placed in each of five bottles of 30 c.c. capacity. Silver nitrate solutions (15 c.c.) of strength  $N/10$ ,  $N/20$ ,  $N/40$ ,  $N/80$ ,  $N/160$  were added respectively to each of the bottles. The bottles were closed and shaken; they were kept overnight at the laboratory temperature in a thermostat. The strength of the solutions after adsorption was determined by titration against sodium chloride of known strength. The weight of the silver ion adsorbed per g. of the adsorbent was calculated.

*Zinc Sulphate.*—Similarly the adsorption from zinc sulphate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) from solutions of different concentrations was determined as above. The zinc was estimated by titration with potassium ferrocyanide using diphenylamine as an indicator. The data are given in the following table.

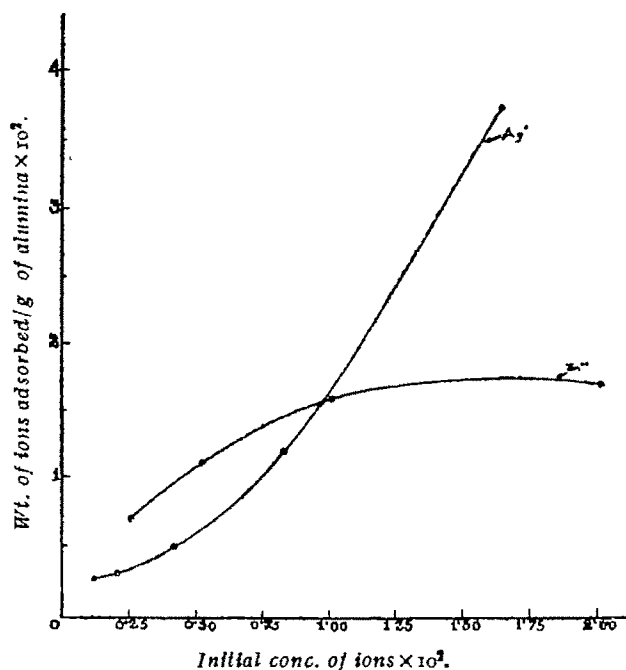
TABLE I

Strength of solution.			Strength of solution		
Before adsorption.	After adsorption.	Amt. of ion adsorbed Wt. of adsorbent	Before adsorption.	After adsorption	Amt. to ion adsorbed Wt. of adsorbent
Silver nitrate.			Zinc sulphate.		
1.021N/10	0.357N/10	0.036	2.13N/10	1.61N/10	0.017
0.511	0.295	0.012	1.06	0.58	0.016
0.256	0.165	0.005	0.53	0.21	0.011
0.128	0.076	0.003	0.27	0.06	0.007
0.064	0.014	0.003			

In Fig. 2, the amounts of ion (+) adsorbed per gram of alumina are plotted against initial ionic concentrations of respective solutions. It is seen that at lower concentrations there is a greater adsorption of zinc ions per g. of the adsorbent than the

silver ions, while at higher concentrations more of silver is adsorbed than zinc. Therefore the preferential adsorption of zinc over silver at lower concentrations is responsible for the reversal of the chromatographic order.

FIG. 2



The results are only qualitative but this suggests a method of separating copper and silver and estimating them in an alloy of copper and silver. Otherwise Cu-Ag with ammonium sulphide give more or less similarly coloured bands and the line of separation is not very clear.

DEPARTMENT OF TECHNICAL CHEMISTRY,  
COLLEGE OF ENGINEERING, GUINDY, MADRAS.

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## INDICATORS IN TITRATIONS WITH CERIC SULPHATE

By T. K. S. MURTHY AND Bh. S. V. RAGHAVA RAO

Crystal violet, a commercial dye, has been shown to be suitable in titrations with ceric sulphate. Its range of usefulness is great compared with other indicators. Comparative studies on other indicators, viz., Xylene cyanol FF, *N*-phenylanthranilic acid and Rhodamine 6G are reported, extending their use to titration other than those originally recommended.

In spite of the excellence of ceric sulphate as a reagent in oxidimetry, its use has not become widespread through absence of suitable and readily available indicators. Willard and Young (*J. Amer. Chem. Soc.*, 1933, **55**, 3260) employed *ortho*-phenanthroline-ferrous complex with great success in a variety of reactions with this reagent, but its use is largely handicapped by its scarcity. Other indicators with a limited application have been reported by various investigators, chief amongst which may be mentioned the following. Xylene cyanol FF by Mitchell and Ward ("Modern Methods in Quantitative Chemical Analysis", 1932); *N*-phenylanthranilic acid by Suerokomoski and Stepin (*J. Amer. Chem. Soc.*, 1936, **58**, 9287). More recently one of us (*Curr. Sci.*, 1947, **16**, 378) reported the use of Rhodamine 6G and its application appears to be more extensive than originally reported. During an extended series of investigations on suitable indicators we have noticed that Crystal violet, a commercial dye, possesses a range of usefulness far greater than any indicator we know of, with the exception of ferrous-phenanthroline complex; besides, its colour change, green to orange-red, is not only easily detectable but very sharp. Our investigations have also disclosed that *N*-phenylanthranilic acid (*loc. cit.*) may be employed in the titration of a number of other substances (*vide infra*), particularly trivalent antimony, in the presence of iodine monochloride; in the latter case excellent results are obtained if the indicator is added towards the end of the titration.

We have further carried out comparative studies on some of these indicators. Table I summarises our results. The titration of either oxalic acid or arsenious acid has not been successful. Xylene cyanol FF has been found unsuitable except in the originally recommended titration of ferrous iron and the end-point is very sharp only if the acid content of the solution does not exceed 0.5N.

It has further been found that ferrous iron may be titrated accurately in the presence of oxalic acid by Xylene cyanol FF and Crystal violet, provided the acid concentration is not above 1.0N and sufficient quantity of phosphoric acid is added, as is evident from Table IIb. With the former indicator, however, colour change towards the end is slow. This last observation is in conformity with the findings of Ferri (*Quart. Jour. & Year-book Pharm.*, 1937, **10**, 351).

TABLE I

Ceric sulphate = 0.05N. Total vol. = 100 c.c. Overall acidity = 0.8N in HCl or  $H_2SO_4$ . Indicator = 3-4 drops of 0.1% aqueous solution of crystal violet.

Amount taken.	* Amount found with		
	Crystal violet.	Rhodamine 6G.	Phenylanthranilic acid.
1. Ferrous ammonium sulphate.			
0.1203 g	0.1203 g.	0.1203 g.	0.1203 g
0.1928	0.1928	0.1928 g	0.1928
0.3855	0.3855	0.3855	0.3855
0.7710	0.7710	0.7710	0.7712
2. Ferric chloride after reduction with $SnCl_2$ .			
0.1123 g.	0.1124 g.		0.1124 g.
0.1235	0.1236	Not suitable.	0.1237
0.2470	0.2470		0.2470
3. Hydrogen peroxide.			
0.00783 g.	0.00783 g.	0.00783 g.	0.00783 g.
0.0162	0.0162	0.0162	0.0162
0.0324	0.0324	0.0324	0.0324
4. Uranyl acetate after reduction with Zn and HCl.			
		(a)	(a)
0.1196 g.	0.1200 g.	0.1200 g	0.1200 g.
0.1622	0.1622	0.1622	0.1622
0.2392	0.2396	0.2400	0.2400
5. Potassium ferrocyanide.			
			(a)
0.0412 g.	0.0412 g.	0.0412 g.	0.0412 g.
0.1000	0.1002	0.1005	0.1005
0.2000	0.2002	0.2000	0.2002
6. Hydroquinone.			
		(a)	
0.0146 g	0.0146 g.	0.0146 g.	0.0146 g.
0.0151	0.0151	0.0151	0.0151
0.0302	0.0302	0.0302	0.0302
7. Stannous chloride.			
			(a)
0.0561 g.	0.0560 g.	0.0561 g.	0.0560 g.
0.0605	0.0608	0.0605	0.0603
0.1210	0.1210	0.1212	0.1212
8. Antimony (trivalent). ( $Sb_2O_3$ ).			
(5 c.c. of 0.005M-ICl added and titrated at 50°).			
			(a)
0.0190 g.			0.0191 g.
0.0205	Unsuitable.	Unsuitable.	0.0205
0.0410			0.0412

The indicator is added towards the end.

\* Each figure represents an average of four titrations

(a) Signifies the indicator has been employed for the first time in this titration.

TABLE IIA

*Titration of Mohr's salt in presence of oxalic acid.*

Ferrous ammonium sulphate taken = 0.3885M. Indicator = Crystal violet. Total volume = 100 c.c.

Overall acidity.	Oxalic acid added	Mohr's salt found.	Remarks.
0.5N	0.0252 g.	0.04008 g.	The reaction is slow towards the end.
"	0.0504	0.4075	
"	0.0756	0.4075	
"	0.1080	0.4080	
"	0.1260	0.4090	
"	0.1512	0.4090	
1.0	0.0252	0.4180	End-point is sharp. Titration not successful.
2.0	0.0252	—	

TABLE IIB

*Titration of Mohr's salt in the presence of oxalic acid on addition of phosphoric acid.*

Total vol. of the soln. = 100 c.c. Syrupy phosphoric acid (d 1.8) added = 5 c.c.

Mohr's salt found with						
Amount of Mohr's salt taken.	Overall acid concn. in HCl.	Amount of oxalic acid added.	Crystal violet.	Rhod-6G.	Phenyl-anthranilic acid.	Xylene cyanol FF.
0.1406 g.	0.8N	0.053 g.	0.1406 g.	0.1427 g.	0.1417 g.	0.1406 g.
"	2.0	0.053	0.1427	0.1427	0.1427	0.1427
0.3855	0.5	0.13	0.3855	0.3887	0.3887	0.3856
"	1.0	0.13	0.3855	0.3920	0.3887	The end-point is not detectable.
"	"	0.26	0.3855	0.3920	0.3902	
"	"	0.32	0.3855	0.3920	0.3902	
0.7710	1.0	0.32	0.7710	0.7780	0.7760	
"	"	0.64	0.7710	0.7780	0.7769	
"	"	1.28	0.7710	0.7769	0.7769	

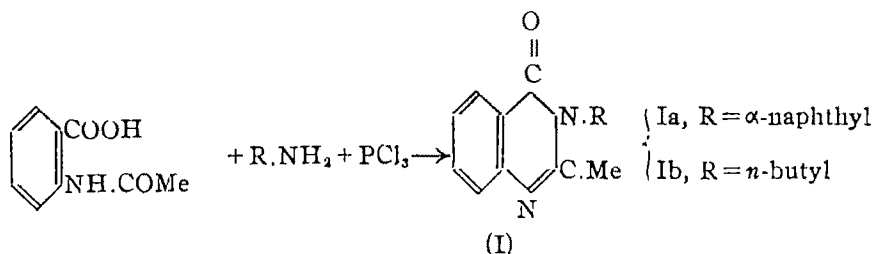
Besides, it appears to be a prerequisite in practically all titrations with ceric sulphate, employing reversible indicators, that the strength of the titrant is not higher than 0.05N, and the overall acidity with respect to hydrochloric acid or sulphuric acid lies between 1N and 2N. Further, in many cases a large excess of the titrant oxidises the indicator irreversibly or at any rate, its sensitiveness largely impaired.

# SYNTHESIS OF 4 QUINAZOLOLS. PART II

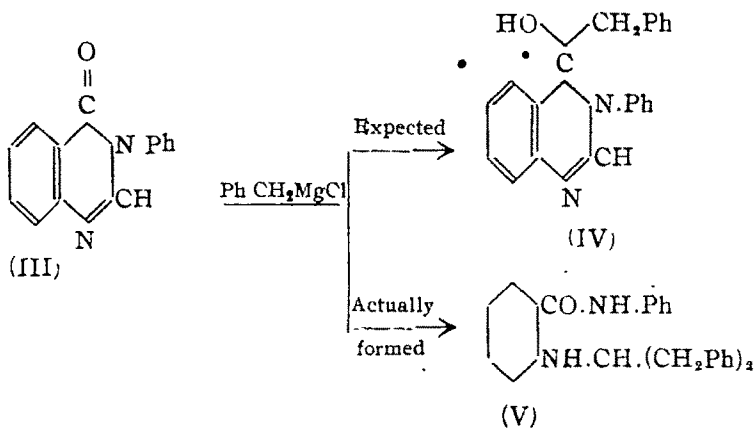
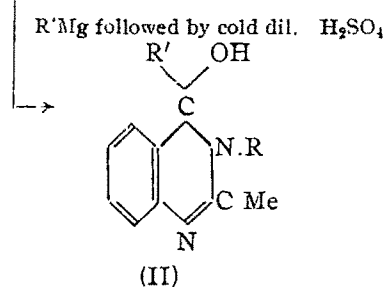
By A. B. SEN AND M. P. UPADHYAYA

Two new 4 quinazolones have been prepared from which seven 4-quinazolols have been obtained with a view to testing them for possible analgesic action

In a previous communication (Sen and Sidhu, this *Journal*, 1948, 25, 437) the preparation of 2-methyl-3-phenyl-4-quinazolone and its conversion into three 4-substituted quinazolols were reported. In this paper the work has been extended to the preparation of 2-methyl-3- $\alpha$ -naphthyl- and 2-methyl-3-*n*-butyl-4-quinazolones from which seven 4-quinazolols have been obtained by the action of different alkyl or aryl magnesium halides on the quinazolones, followed by decomposition of the Grignard complex with dilute acid. The 4-quinazolones were prepared by following the general method of Grimmel, Gunther and Morgan (*J. Amer. Chem. Soc.*, 1946, 68, 548).



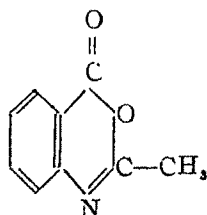
	R =	R' =
II a,	$\alpha$ -naphthyl	<i>n</i> -propyl
b,	"	<i>n</i> -butyl
c,	"	phenyl
d,	"	<i>p</i> -tolyl
e,	<i>n</i> -butyl	<i>n</i> -propyl
f,	"	phenyl
g,	"	<i>p</i> -tolyl



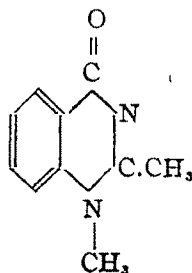


Koelsch (*J. Amer. Chem. Soc.*, 1945, **67**, 1718) studied the action of benzylmagnesium chloride on 3-phenyl-4-quinazolone (III) and has established that the expected 4-quinazolol (IV) is not formed. The reaction follows an anomalous course and results in the formation of the open-chain *N*-( $\beta\beta'$ -diphenylisopropyl)-anthranililide (V).

The question arises whether the reaction products obtained by the action of different Grignard reagents on 4-quinazolones, as reported in this paper and the previous paper (Sen and Sidhu, *loc. cit.*), are the normally expected 4-quinazolols or the open-chain compounds formed by rupture of the heterocyclic ring as in the above case. Koelsch (*loc. cit.*) has drawn attention to the fact that benzylmagnesium chloride reacts with acetanthranil (VI) and with 1:2-dimethyl-4-quinazolone (VII) to give the normally expected alcohols.



(VI)



(VII)

He has offered an explanation of this fact by the development of electrophilic centres at different carbon atoms in the molecule. In compound (III) the electrophilic centre develops at  $C_2$  and attack by  $R^-$  (of  $R-Mg Br$ ) takes place at  $C_2$  in preference to  $C_4$ . In (VI) and (VII)  $C_4$  retains electrophilic properties greater than  $C_2$  and hence the normal course of the Grignard addition at  $C_4$  is followed.

The quinazolones studied by us are all substituted at  $C_2$  like (VI) and (VII) and no electrophilic centre other than at  $C_4$  can be developed. Hence the reaction of the Grignard reagent was expected to follow the usual course. The compounds obtained gave salts with aqueous acids and were also acetylated by acetic anhydride in presence of pyridine.

#### EXPERIMENTAL

*N*-Acetylanthranilic acid was prepared by the action of acetic anhydride on the acid suspended in benzene (Kauffmann, *Ber.*, 1909, **42**, 3482).

**2-Methyl-3- $\alpha$ -naphthyl-4-quinazolone.**—*N*-Acetylanthranilic acid (17.9 g., 0.1M),  $\alpha$ -naphthylamine (14.3 g., 0.1M) and toluene (175 c.c.) were taken in a 500 c.c. three-necked flask, fitted with a mechanical stirrer, condenser and a dropping funnel and heated in a paraffin-bath (130°). Phosphorus trichloride (4.6 g.) in toluene (25 c.c.) was added through the dropping funnel during a period of 15 minutes and the contents refluxed for 2 hours, after which they were transferred to a two-litre distillation flask and basified with 10% sodium carbonate solution (200 c.c.). The toluene was removed by steam distillation and the residue filtered and washed thoroughly with water and finally

recrystallised from alcohol, m. p.  $152^{\circ}$ , yield 27 g. (Found: C, 79.0; H, 4.6; N, 9.2.  $C_{11}H_{14}ON_2$  requires C, 79.7; H, 4.89; N, 9.79 per cent).

*2-Methyl-3-n-butyl-4-quinazolone* was obtained from N-acetylanthranilic acid (59.6 g.), *n*-butylamine (24.3 g.) and phosphorus trichloride (14.2 g.) in the same way. The residue after removal of toluene was transferred to a separating funnel and extracted with ether. The ethereal layer was separated and dehydrated over calcium chloride. The ether was then removed and the residue distilled under reduced pressure, when a product distilling at  $250^{\circ}$  under 8 mm. pressure was obtained, yield 17 g. (Found: C, 72.0; H, 7.1; N, 12.77.  $C_{13}H_{16}ON_2$  requires C, 72.2; H, 7.4; N, 12.96 per cent).

*Substituted Quinazolols.*—The quinazolols were obtained by the action of appropriate Grignard reagents on the quinazolones in the following way.

The Grignard reagent was prepared from magnesium (0.02*M*) and the alkyl or aryl halide (0.02*M*) in the usual way. The Grignard reagent was then cooled in ice and the quinazolone (0.02*M*) suspended in ether was added dropwise. The reaction was over in about 15 minutes after which the contents were refluxed for 2 hours over a water-bath and then decomposed with dilute sulphuric acid. The resulting substance was filtered, washed with water and dried. Most of the quinazolols were recrystallised from alcohol. 3-*n*-Butyl-, 4-phenyl-, 4-propyl- and 4-*p*-tolyl-4-quinazolols were obtained at first as resinous substances which were crystallised with great difficulty from chloroform.

In this way the following quinazolols were obtained.

TABLE I

4-Quinazolols.	M.p.	Yield.	Carbon		Hydrogen		Nitrogen		M. p. of acetyl deriv.
			Found.	Calc.	Found.	Calc.	Found.	Calc.	
2-Methyl-3- $\alpha$ -naphthyl-									
-4- <i>n</i> -propyl-	190°	70.5%	79.6%	80.0	6.35%	6.6	8.3%	8.48	145°
-4-phenyl-	210°	80.3	82.25	82.4	5.2	5.49	7.5	7.69	145°
-4- <i>n</i> -butyl-	162°	87.2	80.1	80.23	6.7	6.97	8.0	8.14	95°
-4- <i>p</i> -tolyl-	172°	66.1	82.3	82.5	5.7	5.8	7.19	7.4	150°
2-Methyl-3- <i>n</i> -butyl-									
-4-phenyl-	165°	85.0	77.35	77.5	7.3	7.48	9.4	9.52	105°
-4- <i>n</i> -propyl-	170°	86.7	73.65	73.84	9.1	9.23	10.6	10.76	—
-4- <i>p</i> -tolyl-	162°	47.0	77.3	77.5	7.2	7.48	9.4	9.52	—

CHEMISTRY DEPARTMENT,  
LUCKNOW UNIVERSITY,  
LUCKNOW.

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## SUPERSATURATION LIMITS OF SOLUTIONS. PART VI. AN ANOMALOUS BEHAVIOUR OF THE PERCHLORATES OF POTASSIUM AND AMMONIUM

BY RAM GOPAL

The spontaneous crystallisation of supersaturated aqueous solutions of barium, sodium and ammonium perchlorates has been studied. It is found that though the solubilities of these perchlorates differ widely,  $T_s - T$  does not change very much with prolonged heating and, taken separately,  $T_s - T$  is almost a constant for the same solute irrespective of the saturation temperature. The low preheating effect in these electrolytes, as well as in  $\text{KClO}_4$ , is probably due to large apparent equivalent volume of these electrolytes; besides, the symmetrical nature of the perchlorate ions and its large apparent ionic volume appear to play an important role.

In an earlier communication (this *Journal*, 1947, 24, 284) the anomalous character of the perchlorate of potassium was pointed out to be an exception to the general rule ( $c\phi$ ) suggested to explain the behaviour of supersaturated solutions towards spontaneous crystallisation on prolonged and continuous heating. In spite of the fact that the rule was found to hold good or its failure satisfactorily explained, in about thirty cases (cf. Bose and Chatterji, this *Journal*, 1949, 26, 94, where the rule has been extended to non-aqueous solutions), it was not even approximately obeyed by  $\text{KClO}_4$ . Apparently no flaw could be detected in the viscosity measurements which were made by the well known method of Scarpa as modified by later workers. The reliability of the apparatus was checked by determining the viscosity of 10% and 20% sugar solutions with its help and comparing the results with the standard values given in the literature which were found to agree within the experimental error. Therefore,  $\eta$  and hence  $\phi$  or  $c\phi$  values of  $\text{KClO}_4$  solutions must be relied upon. Consequently it was considered desirable to examine the behaviour of other perchlorates in order to ascertain the real factor controlling spontaneous crystallisation in these systems.

## EXPERIMENTAL

The available perchlorates, i.e.  $\text{NH}_4\text{ClO}_4$ ,  $\text{NaClO}_4$  and  $\text{Ba}(\text{ClO}_4)_2$ , were recrystallised from conductivity water and dried. The general method used for determining the limits of supersaturation was the same as described in the first paper of this series (*ibid.*, 1943, 20, 183) and the results obtained are recorded in Table I. The data for  $\text{KClO}_4$  have also been given for comparison.

TABLE I

Ammonium perchlorate.		Sodium perchlorate.		Barium perchlorate.		Potassium perchlorate.	
$T_s$ .	$T_s - T$ .	$T_s$ .	$T_s - T$ .	$T_s$ .	$T_s - T$ .	$T_s$ .	$T_s - T$ .
54°	8-9	92-94°	20	51-53°	9	30°	6.4
60-61	8-9	85-86	19	60-63	9	35	6.6
72-73	11-12	87-88	18	53-55	7	40	6.2
81-82	11-12	79-81	19	66-67	8	45	6.0
57-58	9-10	63-65	19	66-68	7	50	6.4
		75-76	20	71-73	9	55	6.5
				83-85	14(?)	60	6.6

The values of  $T$ , the temperature of spontaneous crystallisation, have been omitted for the sake of brevity. It may be mentioned, however, that they do not vary appreciably with heating and therefore they belong to the same class where heating effect is negligible.

## DISCUSSION

Table I clearly shows that in all the perchlorates studied here, the temperature of spontaneous crystallisation is, in general, almost a constant or only changes very slightly from the mean value (cf. lines below the table).  $\text{KClO}_4$  is only slightly soluble, whereas the solubilities of  $\text{NaClO}_4$  and  $\text{Ba}(\text{ClO}_4)_2$  are very high. The low solubilities of  $\text{KClO}_4$  and  $\text{NH}_4\text{ClO}_4$  will give small values of  $c\phi$ , whereas high solubilities of  $\text{NaClO}_4$  and  $\text{Ba}(\text{ClO}_4)_2$ , will, inspite of high viscosity (hence smaller  $\phi$  values), result in large  $c\phi$  values. Hence, although it is possible to explain the low preheating effect in the latter two cases, it is impossible to explain the similar behaviour of the former substances on this ground. We must therefore look for a more widely embracing factor which controls spontaneous crystallisation in these solutions.

Apparent ionic volume,  $\phi_v$ , of ions may be tried as a possible solution, for it will necessarily be involved in the formation of a nucleus of any required size. According to Fajans and Johnson (*J. Amer. Chem. Soc.*, 1942, **64**, 674)  $\phi_v$  of  $\text{ClO}_4$  ion, at infinite dilution, is by far the largest of almost all the common ions, and may therefore be responsible for the above mentioned peculiar behaviour of perchlorates. As supersaturated solutions are, in general, highly concentrated, the combined effect of both the cation and anion, *i.e.* apparent equivalent volume of the electrolyte concerned, at these concentrations, will not be given by the additivity law which may be expected to hold good at infinite dilutions (cf. Fajans and Johnson, *loc. cit.*). It is therefore necessary to find out apparent equivalent volume  $\phi_v$  of different electrolytes in highly concentrated solutions and then values for perchlorates may be compared with those for other electrolytes possessing either negligible heating effect e.g.  $\text{KI}$  and  $\text{KNO}_3$ , or, marked heating effect, e.g.  $\text{BaCl}_2$  and  $\text{Ba}(\text{NO}_3)_2$  etc. This might be expected to yield necessary information.

In Table II are given the  $\phi_v$  values of saturated solutions, calculated from density data given in the International Critical Tables (1928, 3, 104). Saturation temperature, wherever possible, has been chosen to be  $25^\circ$  and the exceptions are properly marked out.

TABLE II

Temperature =  $25^\circ$ .

	Perchlorates of							
	KI*.	KNO <sub>3</sub> .	Na**	K.	NH <sub>4</sub> .	Ba***	BaCl <sub>2</sub> .	Ba (NO <sub>3</sub> ) <sub>2</sub> .
Apparent equiv. volumes	49.62.	42.10	49.83	48.17	62.31	60.02	19.6	22.84

\*  $24.3^\circ\text{C}$ ; \*\*  $50^\circ\text{C}$ , \*\*\*  $20^\circ\text{C}$ .

Table II clearly shows that from the point of view of apparent equivalent volume the perchlorates are very like KI and  $\text{KNO}_3$  and widely different from  $\text{BaCl}_2$  and  $\text{Ba}(\text{NO}_3)_2$ , and therefore, if this property at all influences or plays any part in the phenomenon of spontaneous crystallisation, the perchlorates should behave like KI and  $\text{KNO}_3$ , and not like  $\text{BaCl}_2$  and  $\text{Ba}(\text{NO}_3)_2$ .

The significance of a large ionic volume may be considered here in some detail. For a particular temperature  $T$ , the stable crystal nucleus must be of a definite size in order to avoid its own dissolution and keep intact its activity to start spontaneous crystallisation. The process will entail the coming together of a number of lattice forming units, whether simultaneously or developed catalytically (Harbury, *J. Phys. Chem.*, 1947, **51**, 382) from single molecules or ions, is immaterial. The particular size is more easily attained, the larger the volume or size of the constituent ions, the smaller the number of ions or molecules will be required to make it up. Hence, although the  $c\phi$  values of  $\text{KClO}_4$  and  $\text{NH}_4\text{ClO}_4$  are small, they are compensated by a large volume of the lattice forming units resulting in an easy formation of an active crystal nucleus even when heating has deactivated or immobilised many catalytic agents. Thus the number of successful collisions will be sufficient to start spontaneous crystallisation. Furthermore, the symmetrical nature of the perchlorate ion also helps in the formation of the active crystal nucleus. Ephraim ("Inorganic Chemistry", 1939, p. 376) remarks that "the general properties of the perchlorates depend to a large extent on the great atomic volume and the symmetrical nature of the perchlorate ion". That appears to account for the peculiarity of the perchlorates towards prolonged heating as well.

A large ionic volume also promotes, in general, a low hydration. Thus, a large  $\phi$ , also serves to keep the ions free from the water molecular envelope surrounding them and this will naturally help in an easy formation of a germ crystal. Consequently, a large ionic volume of the perchlorate ion helps spontaneous crystallisation in this indirect manner also.

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## INDUSTRIAL DEVELOPMENT OF INDIA—PRESENT AND FUTURE\*

By J. N. RAY

It is customary for the President of the Society to select for his annual address a topic in which he is a specialist. I would make a slight departure from the accepted practice and would like to talk on a subject which is uppermost in the minds of all chemists in this country, namely, "Industrial Development of India—present and future". This topic would be in harmony with the aims and objects of the Society, which are primarily to encourage and foster the spirit of enquiry and original research, to protect and develop scientific life in this country and to promote the growth of cultural fellowship among chemists in general.

Under the Government of India Act 1935, the development of industries was a Provincial subject, but it was open to the Central Government to declare by law that the development of certain industries under Central control was expedient in the public interest. On such a declaration being made, the development of such industries could become a Central subject. No such action was, however, taken with the result that at the outbreak of hostilities in 1939, the development of industries remained wholly a provincial subject. The war necessitated central control and direction over industries, as India was the supply base for the armies in the Middle East and the Far East. The Eastern Group Supply Council, which was formed as a result, placed on India all demands which could be met from India. The Central Government naturally took upon themselves the responsibility for the supply of entire requirements of the Indian army, both at home and abroad. To discharge this onerous responsibility, it was found necessary to create the Department of Supply which was responsible not only for all the procurement activities of the Government but also for developing new capacity. A large number of scientific men were thus mobilised for discharging these responsibilities. How well this duty was performed could be gauged from the fact that during the years 1942-1946, 106 crores of rupees worth of chemicals, paints, gases and petroleum products were procured. The purchases on account of leather and tanned materials amounted to 23 crores of rupees, that of rubber items to 10 crores, and so on.

With the cessation of hostilities, the Government of India felt that this development which had taken place during the war should be stabilised and put on a firm basis. It was recognised that India's industrial development would have to be the result of conscious and deliberate planning and should not be left to haphazard and unco-ordinated efforts of private industrialists. In 1945, the Government of India made an important statement of India's industrial policy. In this, it was recognised that positive steps to encourage and promote the rapid industrialisation of the country to the fullest possible extent were an inescapable responsibility of the Government. A number of

\* Presidential address delivered at 26th Annual General Meeting of the Indian Chemical Society, held on January 3, 1950 at Poona.

Panels were set up to report on the existing position of various industries. The general directive to the Panels was on the following lines :—

- (i) The panels should report on the scope and extent of development including the types of products which should be taken up for development either by private enterprise or by the State ;
- (ii) The extent to which technical advice from abroad may be necessary ;
- (iii) The availability and future requirements of technical personnel ;
- (iv) The manner and degree of co-operation with foreign firms considered necessary and desirable ;
- (v) Location of the industry and assistance required from Government in the development of industries, and the
- (vi) Stages in which industry should be developed.

The recommendations submitted by the Panels were considered by the Government of India in consultation with the Provincial authorities, and certain targets of production and expansion of capacity were accepted.

In the meantime, with the cessation of hostilities, the Department of Supply was amalgamated with the Department of Industries & Civil Supplies, and the new Department of Industry & Supply was created. The executive responsibility for carrying out the accepted recommendations of the various Panels was transferred to this new Department of Industry & Supply.

It will now be worthwhile to make a brief survey of the various developments that have taken place in the field of industry and also to indicate those that remain to be done.

The chemical industry occupies a key position in the economy of every country. Its products are used in a number of other industries such as Textiles, Paper, Leather, Soap, Glass, Ceramics, Paints, Plastics, Rayon, etc. The chemical industry, in India, in its modern form, really began after World War I (1914-18), although the oldest chemical factories were established in the middle of the last century. It was during World War I that real development took place. In 1921, there were 14 large chemical works employing 2500 workers. By 1939, the number of works rose to 38 employing about 8000 people. At present there are 200 firms employing 25,000 men.

*Sulphuric acid.*— There are now 40 firms, which can produce about 150,000 tons of sulphuric acid in 43 units. Of these, 11 are contact process units, mostly installed in the postwar period. The following table shows the consumption of sulphuric acid industry-wise :—

Chemicals	...	...	..	...	40%
Fertilisers	...	...	..	...	40
Metals	...	...	.	...	5
Cotton textile	...	...	...	...	5
Mineral oil	...	...	...	...	2
Leather	...	...	...	...	1
Engineering & other industries	...	...	...	...	7
					<hr/>
					100

Four units are under erection, which would give an additional capacity of another 30,000 tons.

*Superphosphate.*—The production of superphosphate was negligible before



the war. At present, capacity exists for the production of 90,000 tons of superphosphate per annum and with the expansion schemes now in hand, it is expected that by the end of 1950, the production would reach the target figure of 100,000 tons per annum. The Government now purchases all superphosphate at a fixed price. This has helped considerably in increasing indigenous production.

*Ammonium sulphate.*—The Government of India decided that ammonium sulphate should be produced by the State on a large scale. A Commission was appointed in 1945 to report on the possibility of manufacture of ammonium sulphate in India. As a result of the recommendations made by this Commission, it was decided to start the production of ammonium sulphate at Sindhri with a capacity of 350,000 tons per annum. This factory is nearing completion and will be one of the biggest units in the world. There are two other units producing synthetic ammonia, one at Mysore and the other at Travancore, with an aggregate capacity of 56,000 tons per annum. The production of sulphate from the ammoniacal liquors of the coke ovens is 22,000 tons.

*Bichromates.*—India's production capacity now is 3000 tons per annum and the domestic consumption is only 1000 tons. We have a large exportable surplus and considerable quantities have been exported abroad.

*Soda ash.*—India's requirements of soda ash are about 120,000 tons per annum for her various industries.

Glass industry	...	...	30,000 tons
Silicates	...	...	15,000
Textiles	...	..	9,000
Paper	..	...	5,000
Chemical industry	...	...	6,000
Misc. requirements	...	...	10,000
Washing	...	...	45,000

Total 120,000

The present installed capacity is 54,000 tons. The chief difficulty in bridging this gap between production and domestic consumption is that of obtaining industrial salt at a reasonable price. The ideal location for the soda ash industry is naturally the coalfields which are situated a long way off from the Western coast, where cheap sea salt is available or from the salt-beds of Rajputana. The cost of transport is the principal limiting factor in the development of the soda ash industry.

*Caustic soda.*—India's requirements of caustic soda are 70,000 tons per annum, of which the soap industry consumes 31,500 tons, the textile industry, 19,250 tons, the paper industry 10,500 tons and other miscellaneous industries, 8,700 tons. The present installed capacity is 13,500 tons. There are certain units which are producing their own requirements of caustic soda and this capacity would come to another 3000 tons. At present, 3 units are under erection, which will give an additional capacity of 10,000 tons.

*Liquid chlorine.*—India has an installed capacity of 6,400 tons for the production of liquid chlorine. This is more than sufficient to meet all internal demands, but the difficulty is transport. Long distances involved stand in the way of free transport of liquid chlorine from the factories to places of consumption. Recently, a firm has planned the production of high test hypochlorite.

*Bleaching powder.*—India produces 5,160 tons of bleaching powder and plans for expanding the capacity are in hand.

*Bromides.*—From the bitterns in the manufacture of salt, India has now established a capacity for the manufacture of 200 tons of bromides. The internal consumption has been computed to be 60 tons. There is ample scope for catering to the export market.

*Magnesium chloride.*—Another by-product in the manufacture of salt is magnesium chloride. India is not only able to meet her internal demands but has been exporting magnesium chloride to various countries including U.K.

*Magnesium sulphate, alum, etc.*—The demands for these chemicals are being fully met. There is also some export trade in these chemicals.

*Potassium chlorate.*—The match industry in India has expanded phenomenally during the last few years. At present, the country's aggregate capacity for the production of matches is 40 million gross boxes. We are also having a flourishing export trade in matches. To cater to the needs of the match industry we require a production of 2,000 tons of potassium chlorate. We are now mostly able to meet all internal demands for potassium chlorate.

*Fine chemicals and pharmaceuticals.*—The war found India totally unprepared to meet the growing needs of the Army. The procurement of medical stores for Government hospitals and the Army was the responsibility of the Director-General (I. M. S.), who was the head of the Medical Stores Department. The Medical Stores Department functioned primarily to supply the Army with all its medical and veterinary stores such as drugs, dressings, surgical instruments, etc. In addition to supplying the needs of the Army, the Medical Stores Department also provided for the needs of most of the Provincial Government and semi-Government hospitals, certain railways, mission hospitals, municipal institutions and other local bodies. The Medical Store Depots in India were the biggest importers of drugs and other medical stores and they were also manufacturers of drugs and dressings. There were five medical store depots maintained in five large centres in India. Two medical store depots had factories attached to them where certain preparations were made. These factories were at first located at Lahore and Calcutta but later on they were shifted to Madras and Bombay. At the outbreak of World War II, it was quickly realised that owing to shipping restrictions, these medical store depots would have to play a very large part in supplying to the growing needs of the Army, both at home and abroad. The organisation of the Director-General (I. M. S.) was strengthened by the recruitment of two officers, who were placed in charge of the production of Drugs and Dressings and Surgical Instruments and Appliances respectively. The result of intensive effort to increase production of medical stores was that the value of medical stores purchased in India (exclusive of depot manufactured articles) rose from Rs. 15.8 lakhs in 1938-39 to Rs. 3.48 crores in 1942-43.

Drugs and accessories needed for the Army could be roughly classified under the following headings.

- |                                      |                                  |
|--------------------------------------|----------------------------------|
| (i) Galenicals                       | (vii) Special type of glassware. |
| (ii) Drugs of natural origin         | (viii) Rubber goods              |
| (iii) Vitamins and hormones          | (ix) Surgical dressings          |
| (iv) Synthetic drugs                 | (x) Ligatures                    |
| (v) Purified basic chemicals         | (xi) Vaccines and sera           |
| (vi) Laboratory stains and chemicals | (xii) Anti-biotics.              |

India's requirements of galenicals were entirely met from indigenous sources. Surgical dressings, vaccines and sera, rubber goods, laboratory stains and chemicals were produced on a large scale. Of the drugs of natural origin, Morphine, Codeine, Strychnine, Caffeine, Ephedrine, Santonin, Quinine were produced in sufficient quantities not only for meeting internal demands, but, in some cases, for purposes of export. India's position regarding synthetic drugs was unsatisfactory, because the basic intermediates were in most cases unavailable. It was, however, possible to produce synthetically a very large number of drugs. A number of antiseptics and disinfectants, purgatives, uric acid solvents, vaso-constrictors, vaso-dilators, antipyretics, analgesics, narcotics, general anaesthetics and local anaesthetics were successfully produced. It can be said that given the equipment and the intermediate chemicals, there is not a single synthetic drug which is beyond the ability of an Indian chemist to produce.

During the war, an attempt was made to obtain intermediate chemicals. India is now able to produce 2 million gallons of benzene and 1 million gallons of toluene per annum at a cost which compares favourably with that prevailing in other countries. Recently, the manufacture of nitrobenzene at the Ordnance Factories has been established and it is now possible for the Indian industry to obtain about 100 tons of nitrobenzene at a price of Rs. 94/- per cwt. India produced very large quantities of T. N. T. during the war and, in fact, was one of the best sources of supply of this high explosive. It has not been difficult to establish the production of mono-nitrotoluenes which are now obtainable at a reasonable price. Manufacture was established for the production of 1000 tons of acetone from alcohol which is also now available for industrial purposes. During the war, it was felt necessary that the production of power alcohol should be taken in hand. At present, we have a capacity for the production of 14 million gallons of power alcohol in this country. Considerable quantities of butyl and amyl alcohol are also obtainable as by-products in this industry. The Indian coal is generally carbonised at a fairly high temperature with the result that the percentage of naphthalene hydrocarbons is rather high in the distillate. The production of naphthalene has been developed and we have now a capacity of 2000 tons of naphthalene per annum, which is capable of further expansion at a short notice. A certain amount of phthalic acid is also produced. The production of other basic chemicals such as Aniline, Hydroquinol, etc., has also been developed.

The development of the intermediate chemicals industry is closely bound up with the development of finished products. If this vicious circle is to be broken, then it occurs to me that it is necessary that a start should be made at the finished product end. I would not completely rule out a start being made by small units producing intermediate chemicals to feed the concerns producing finished products. It has been

said that the day of small business is over. This is not entirely correct. In the U. S. A., it has been found that a mass production concern is not equipped to handle small order and special jobs. These can be adequately handled by a small outfit which also supplies the needs of the big manufacturers. Even in the field of automobile industry, it has been noticed that a big manufacturer buys nearly 1,100 different items from 400 small firms. In the most specialised industry, namely, the Petroleum Industry, the five largest refining companies in the U. S. A. account for only 40% of the capacity. There are 170 small concerns who have been able to hold their own against the competition of the bigger manufacturers. Similarly 7 big chemical manufacturers depend on 120 small-size firms for many of their requirements. Bigger size does not necessarily mean the greater efficiency.

This was amply borne out during the war, when a small firm produced *para*-aminoacetanilide and supplied successfully all the big manufacturers of organo-arsenicals and organo-antimonials based on *para*-aminoacetanilide. The manufacture of certain types of fine chemical intermediates can easily be undertaken by our chemistry graduates with adequate research experience even on a very small scale. During the war, large quantities of imported commercial dyes were purified and converted into bacteriological stains. In fact, the entire demands for these laboratory stains were met from the supplies made by very small manufacturers.

Following is a list of important drugs which cover the whole field of chemotherapy. Items produced in India are marked with an asterisk.

#### *Antiseptics and Disinfectants*

- |   |                           |
|---|---------------------------|
| *1. Phenol  | 15. Methyl violet         |
| 2. Salol  | †16. Crystal violet       |
| 3. Resorcinol   | 17. Auramine              |
| 4. Guaiacol, Guaiacol carbonate,<br>Guaiacol potassium sulphate | 18. Rivanol               |
| *5. Thymol  | 19. Rhodamine             |
| 6. $\beta$ -Naphthol  | 20. Chinisol              |
| *7. Tribromophenol  | 21. Brilliant Green       |
| 8. Iodoform   | †22. Malachite Green      |
| *9. Formaldehyde  | 23. Trypan Red            |
| *10. Hexamine   | 24. Trypan Blue           |
| *11. Chloramine T   | *25. Mercurochrome        |
| 12. Acriflavine   | *26. Cresol               |
| 13. Dermatol  | *27. Chlorinated xylenols |
| *14. Protargol  | *28. D. D. T              |

#### *Purgatives and Aperitives*

- |                    |                                      |
|--------------------|--------------------------------------|
| 1. Phenolphthalein | 2. Orexin (Phenyldihydroquinazoline) |
|--------------------|--------------------------------------|

#### *Diuretics and uric acid solvents*

- |               |                 |
|---------------|-----------------|
| *1. Caffeine  | 4. Salyrgan     |
| 2. Piperazine | 6. Theophylline |
| *3. Atophan   | 6. Theobromine  |

\* Are produced in India, in many cases, in insufficient quantities

† From imported intermediates.

*Vaso-constrictors*

- |                |                                   |
|----------------|-----------------------------------|
| *1. Adrenaline | 4. Alkaloids of Ergot: Ergotoxin, |
| *2. Ephedrine  | Ergotamine, Ergometrin,           |
| 3. Benzidine   | Ergotinine, Tyramine.             |

*Vaso-dilators*

- |                  |                    |
|------------------|--------------------|
| *1. Amyl nitrite | *3. Nitroglycerine |
| 2. Ethyl nitrite | 4. Octyl nitrite   |

*Antipyretics and analgesics*

- |                   |               |
|-------------------|---------------|
| *1. Aetanilide    | 5. Aspirin    |
| *2. Phenacetin    | 6. Antipyrine |
| 3. Benzoic acid   | 7. Pyramidone |
| 4. Salicylic acid |               |

*Narcotics and General Anaesthetics*

- |                     |                |
|---------------------|----------------|
| 1. Cyclopropane     | *9. Chloretone |
| *2. Ether           | 10. Avertine   |
| *3. Para-aldehyde   | 11. Veronal    |
| 4. Acetophenone     | *12. Luminal   |
| *5. Chloroform      | 13. Sulphonal  |
| 6. Urethane         | 14. Trional    |
| 7. Adaline          | 15. Tetronal   |
| *8. Chloral hydrate |                |

*Local Anaesthetics*

- |                    |                     |
|--------------------|---------------------|
| *1. Ethyl chloride | *4. Cocaine         |
| 2. Anaesthesine    | 5. Eucaine          |
| 3. Novocaine       | 6. Pentothal sodium |

*Antiprotozoal and Antibacterial Drugs*

- |                       |                   |
|-----------------------|-------------------|
| *1. Atoxyl            | 10. Neostibosan   |
| *2. Tryparsamide      | 11. Neocardyl     |
| *3. Carbarsone        | 12. Mercurochrome |
| *4. Neo-salvarsan     | 13. Merthiolate   |
| 5. Stovarsal          | *14. Rmetine      |
| *6. Sulpharsphenamine | 15. Yatren        |
| 7. Solusalvarsan      | 16. Vioform       |
| 8. Mapharside         | 17. Sulpha drugs  |
| *9. Urea Stibamine    | (detailed below). |

*Anti-malarials*

- |                  |                |
|------------------|----------------|
| 1. Equinine      | 4. Mepacrine   |
| 2. Aristochinine | 5. Paludrine   |
| 3. Pamaquin      | 6. Chloroquin. |

\* Are produced in India ; in many cases, in insufficient quantities.

*Sulphanilamide group of Drugs (Sulpha drugs)*

- |                    |  |
|--------------------|--|
| *1. Sulphanilamide | 8. Albucid                               |
| 2. Prontosil       | 9. Dagenan                               |
| 3. Prontosil sol   | 10. Sulphaguanidine                      |
| 4. Proseptazine    | 11. Sulphathiazole                       |
| 5. Soluseptazine   | 12. Sulphapyridine                       |
| 6. Rhodilone       | 13. Sulphadiazine, sulphamerazine        |
| *7. Uleron         | 14. <i>pp'</i> -Diaminodiphenylsulphone. |

*Anti-biotics*

- |                 |                  |
|-----------------|------------------|
| 1. Penicillin   | 3. Chloromycetin |
| 2. Streptomycin | 4. Aureomycin    |

*Miscellaneous Drugs*

- |  |                             |
|--|-----------------------------|
| *1. Camphor                                      | 8. Sulphoform               |
| *2. Ethyl ester of nicotinic acid<br>(coramines) | 9. Solganol                 |
| *3. Glycerophosphates and choline                | 10. Mandelic acid           |
| 4. Cardiazole                                    | 11. S. V. P. 36             |
| 5. Cantharidine                                  | *12. Iodoxyhydroxyquinoline |
| *6. Calcium gluconate                            | *13. Kurchi bismuth iodide  |
| 7. Aulinogen                                     | *14. Emetine { from natural |
|  | *15. Santonine { sources.   |

\* Are produced in India: in many cases, in insufficient quantities.

It will be seen that there is a considerable scope for developing many items of manufacture which are at present not produced in India.

*Development Plans in hand*

We have been considering the question of production of Penicillin and other anti-biotics for a long time. In 1945, the Director-General of Supply financed an investigation for the production of Penicillin on a laboratory scale. Workers at the Institute of Science, Bangalore, and the Haffkine Institute, Bombay, have also been experimenting on the production of Penicillin. In March 1945, advantage was taken of the presence in England of Professor B. C. Guha, then an officer of the Department of Food, and a survey was undertaken by him on behalf of the Department of Supply of manufacture both in the U. K. and the U.S.A. The Department of Planning and Development sent out a team consisting of General Sir Saheb S. Sokhey and Dr. K. Ganapathy to investigate the possibility of manufacturing Penicillin in India. They submitted their report and certain investigations were made on the lines suggested in the Report. It was, however, felt that further investigations were necessary before a decision could be taken. Consequently, the Government of India sent out a second team consisting of General Sokhey, Dr. Ganapathy and Dr. Sankaran for the purpose. It has now been decided that the manufacture of Penicillin would be undertaken as a State enterprise in collaboration with a foreign firm. It is proposed to produce 1200 billion units per annum with a provision to increase it to 3600 billion units, if necessary. In the same factory, it is also proposed to manufacture certain sulpha drugs and synthetic antimalarials.

The collaboration of a foreign firm has been obtained for the production of *para*-aminosalicylic acid, a new curative agent in the treatment of tuberculosis. Certain proposals have been received for the manufacture of Polystyrene required as a raw material for the plastic industry. A scheme for the production of Phenol on a large scale has been worked out and is under examination. A foreign firm is interested in manufacturing this in collaboration with an Indian firm. Three firms have been granted licences for the large-scale production of acetic acid and acetic anhydride. The aggregate production would come to about 3,000 tons per annum, which will be more than sufficient for India's present internal requirements. A large plant for the production of acetate rayon is also under erection. This plant will be producing its own acetic anhydride.

A British firm has already undertaken an extensive survey about the possibility of manufacturing certain industrial explosives. The scheme will be considered by the Government of India as soon as possible.

India consumes about 180 million gallons of motor spirit, 66,000 tons of kerosene, about 30,000 tons of various diesel oils and 53,000 tons of furnace oil every year. The Indian production of motor spirit (natural) is only 15 million gallons, that of kerosene 4000 tons and about 4000 tons of various diesel oils. This is an extremely unsatisfactory position. The Government decided in May 1948 to get from Messrs. Koppers Inc., Pittsburgh a report on the possibility of manufacture of synthetic oil from coal. Messrs. Koppers undertook an elaborate investigation and submitted their report which is now under the consideration of the Government of India. Several other offers have also been received from foreign firms.

An extensive survey was also undertaken about the occurrence of suitable low grade coal required for the purpose. It has been found that extensive deposits are available which can be worked by the strip mining method to give all the coal required for such a project at an economical rate. The low temperature carbonisation of this coal will produce a char suitable as domestic fuel and the tar could be processed to aviation petrol. A part of the char can be used for gasification to produce synthesis gas and also hydrogen needed for the hydrogenation of tar. If such a scheme is adopted, a considerable amount of oxygenated hydrocarbons will be obtained as a by-product which will be admirably suited as a starting material for the preparation of various organic substances used in commerce.

Under the auspices of the Damodar Valley Authority the Governments of Bihar and West Bengal in collaboration with the Government of India brought out some specialists from Germany to report on the possibility of establishing the dyestuff industry in the Damodar Valley area. Other independent investigations were also carried out by some firms. The whole matter is under consideration. Of the various dyes that are largely used in this country, there are a few items which account for a large proportion of our imports of dyestuffs. These are :

- (i) Alizarine group of dyes including vat dyes of the anthracene group.
- (ii) Congo red
- (iii) Rapid fast colours
- (iv) Vat dyes such as Indigo, Carbazol blue, etc.

(v) Sulphur black  
(vi) Metanil yellow

(vii) Rhodamines  
(viii) Chrome colours.

A full investigation has been made of the various quantities of intermediate chemicals that will be needed for the manufacture of these dyes. The analysis shows that it is possible to produce some of these dyestuffs economically in this country, as most of the intermediates will be available from existing or future production of chemicals which has been planned.

Plans are also in hand for the production of Methanol and formaldehyde at Sindhri.

In view of the very large development that has taken place in the production of plastic articles in this country, it is necessary that the manufacture of moulding powders should be taken in hand early. At present only one firm is producing Phenol-formaldehyde resin but not in sufficient quantity. There are now about 40 firms producing plastic articles in India with an aggregate consumption capacity of 3,000 tons of Phenol-formaldehyde resin, 2500 tons of Polystyrene and large quantities of other moulding powders. In view of the importance of phenol as an intermediate for the various industries, such as Dyestuffs, Pharmaceuticals and Plastics, an American firm is considering putting up a plant for the production of phenol.

*Plywood.*—There has been very large development of the production of plywood needed both for the fabrication of tea chests and also for commercial purposes. There are at presents 45 firms producing nearly 80 million sq. feet of plywood for tea chests and about 20 million sq. feet for commercial plywood. The establishment of plastic resins would go a long way to meet the demands for the plywood industry's requirements of various types of resins. Plans have also been formulated for the production of Urea at Sindhri; when the plan materialises, the production of Urea-formaldehyde resin will not be difficult.

*Raw films.*—India is the world's second largest producer of cinema films. It is therefore extremely important that India develops the production of raw films. Co-operation of a Swiss group has been sought for the production of raw films in India.

Mention has already been made about the project for the manufacture of ammonium sulphate at Sindhri. The connected load of the fertilizer factory is, as at present planned, about 45,000 K. W., added to which there is a big demand for steam for process work. In view of the necessity for supplying additional power from Sindhri to the Bihar grid, it was decided to generate 80,000 K. W. at Sindhri with room for expansion to 200,000 K. W. if need be. The various River Valley schemes which are under planning will also need very large quantities of high tension insulators, which are at present not produced in the country. A survey has been undertaken as to the possibility of producing High Tension Insulators in India. The scheme is now under examination.

*Steel.*—The planning for the production of steel is the responsibility of the Engineering Section of the Directorate General of Industries & Supplies, but a brief mention may be made about the position of steel in this country, as the development of chemical group of industries is intimately connected with the question of production of steel. In January 1945, the Department of Planning & Development having provisionally



assessed the immediate postwar steel requirements of India at 3 million tons as against the then production capacity of 1.2 million tons, appointed a committee to investigate the possibility of attaining the target which was provisionally fixed by the Government at 3 million tons. Three firms of international reputation were entrusted with the task of reporting on the possibility of India's attaining this target.

India, one of the very few nations of the world endowed by Nature with an abundant supply of high quality raw materials required for the manufacture of steel and with 20% of the world's population, now has less than 1% of the world's steel production. The present steel expansion plan represents only the initial and immediate step in the ultimate programme to place our country among the major steel producing areas of the world. The three firms entrusted with the task have now submitted their reports which are under examination by the Government of India.

*Cement.*— Closely associated with the requirement of steel is that of cement. India today has got an installed capacity for the production of 2.7 million tons of cement in 21 units. Three new factories are under erection and seven factories are expanding their capacity. It is expected that by the middle of 1950 we will have attained a target of 3.5 million tons. India's present internal consumption is about 4 million tons and with the development of various River Valley Projects, the consumption is expected to go up by another 2 million tons within the next few years.

*Paper.*— India's present production of paper is only 110,000 tons per annum. With the growth of literacy, it is estimated that the consumption of paper will increase considerably. The immediate target to be achieved by 1951 has been fixed at 200,000 tons. Fifteen firms are already producing paper at the rate of 110,000 tons per annum. Six of these firms have decided to expand their capacities by another 50,000 tons. Four new units are coming into production by the end of 1950, with an additional capacity of 43,000 tons. It will, therefore, be seen that the target fixed will be reached in time.

*Leather.*— The export of tanned hides and leather products gives India valuable foreign exchange. India's total foreign exchange earned in this group of products has been in the neighbourhood of Rs. 19 crores per annum. It is, therefore, important to make this industry as self-sufficient as possible with respect to its requirements of chemicals and tanning substances. It has already been mentioned that India is now fully capable of meeting all demands for chromium compounds. The question of producing certain types of Syntans and finishing chemicals is also engaging attention.

*Rayon.*— It has already been mentioned, that one unit for producing acetate rayon is under erection. Two other units will soon be going into production of rayon by the viscose process. Arrangements have been made for the production of carbon bisulphide, caustic soda and other chemicals required for keeping these plants in production. A reed has been found which after processing gives good pulp suitable for use in rayon manufacture. This reed has been found to have as high as 95% of  $\alpha$ -cellulose. Pilot plant trials have been made with regard to the suitability of this reed and if the large-scale trials which are under test succeed, then one of the most important problems facing the rayon industry would be solved.

*Rubber.*— India produces about 18,000 tons of natural rubber per annum. Its consumption in the rubber processing factories has been estimated to be about

20,000 to 22,000 tons. It will therefore seem that we are more or less self-sufficient with regard to our requirements of natural rubber. India now produces all her requirements of tyres and tubes and has also a fairly large exportable surplus. At present, accelerators, vulcanisers and other rubber chemicals are imported. Large quantities of carbon black are required to be imported for this industry. The production of these rubber chemicals is an important necessity which should receive immediate attention. We are importing every year nearly Rs. 3 crores worth of various rubber chemicals and dyes.

It will be seen that the developments mentioned and also others which are in hand will need a considerable amount of capital investment. The Government of India have now declared, in unequivocal terms, the conditions under which they would welcome the participation of foreign firms in the industrial development of India. It is gratifying to note that during the last fifteen months a considerable amount of foreign capital has been invested in India.

Apart from the question of capital formation, the most important requirement of industry is its valuable raw material, namely, technical personnel. The Government of India undertook an investigation of the Scientific Man-power position of the country. Since 1945, a scheme of sending science graduates for training abroad has also been inaugurated. A large number of students have been sent abroad for higher technical training. Owing to the postwar rush of students in the various foreign universities, it has often been found extremely difficult to secure adequate theoretical and practical training for these scholars. It is therefore imperative that the facilities available for technical training in India should be utilised to the fullest extent before a scholar is sent abroad, for further studies. It was suggested that a priority list of subjects should be drawn up and the subjects in which training in India cannot be imparted adequately should be given preference over other subjects. It is recognised that the Universities have been sadly depleted of their teaching personnel on account of the very poor scales of pay that prevail there. As far as I know, there has been hardly any revision of the scales of pay which were fixed after World War I. The cost of living index has gone up by over 300%. Today it is impossible for a university teacher to keep the wolf from the door with the pay which he is offered. He has therefore no option but to seek other avenues of employment. The effect of this diversion of really capable men from the teaching profession will be felt within a few years when perhaps it would be too late to remedy the situation. It is true that a large number of National Laboratories with attractive scales of pay are being established in various subjects but these Laboratories can hardly be expected to fulfil the functions of a University. In England, the National Chemical Laboratory is charged with the responsibility of carrying out research in the national interest for the benefit of the community and to meet the requirements of Government Departments.

According to the Director of Chemical Research Laboratory, Teddington, there are four kinds of work which are suited to the Laboratory's programme :

- (1) Research leading to fundamental reference data of general value.

The universities would hardly be interested in undertaking this sort of an investigation which would require laborious work for a number of years.

(2) New methods and techniques of chemistry in which it is desirable that an expert group should be maintained.

In this group would fall the development of, say, high pressure technique, micro-analysis, radiometry, etc.

(3) Work dealing with the utilization of indigenous raw materials and with the concentration of low grade substances.

(4) The conservation of essential raw materials.

It appears, therefore, that in England, the National Laboratories fulfil definite functions. If a similar plan is adopted for the National Laboratories in India, it will be clear that so far as the general training of a student or initiating him into the methods of research is concerned, the Universities will still have to play their role unaided. It will, therefore, be a great disaster if the Universities get depleted of their talents because of the low scales of pay given to the teachers. There are also a certain number of research establishments specialising in sugar, lac, cotton, etc. maintained by various Government Departments. A considerable difference in the scale of pay of research staff exists in these institutions. The inevitable result of such a disparity is that the best talent tends to gravitate towards that research centre which provides the best terms and conditions of service. This is often not to the best interest either of the worker or of the nation.

It has been stated that the Universities do not have adequate funds at their disposal to better the lot of teachers. But, of late, a tendency to multiply the post-graduate teaching and research departments in the same university has been noticeable. As most of the universities have not adequate funds at their disposal to run the existing departments properly and to bring them to a higher level, such a tendency will have the effect of lowering the general standard of teaching and research. It is not at all necessary for each university to have all conceivable departments of teaching and research. One university can *give more emphasis* to a few subjects and bring them to a higher level leaving other universities to do the same in respect of remaining subjects. It is also necessary that an uniform scale of pay should prevail in the different universities and there should be possibility of interchange of teachers and professors for definite periods.

Apart from the question of pay of University teachers, another handicap of the University worker is the very small research grant he gets to pursue his subject. Even with the best of intentions, it is not possible to do much unless funds are available for procuring equipment and chemicals needed for an investigation. The Board of Scientific & Industrial Research gives grants to some University workers for investigations of specific subjects. Research made to order is not the same thing as research which a worker wishes to pursue on his own accord.

Attempts have also been made to import foreign technicians to meet the requirements of industry for specialists. 37 German technicians have been brought

out to India with the help of Directorate General of Industries & Supplies for various industries. Eighteen more technicians will shortly be arriving in India. Besides these, certain British, American and Japanese technicians have also come out to India. As a condition precedent to allowing a foreign firm to operate in this country, it has been stipulated that the Indian personnel should be trained to take up full charge of the industry within a definite period. All these are palliative measures. But it is to be recognised that the technicians will have to be trained within the country. We cannot depend for ever on technical help from outside. It is, therefore, all the more important that the present anaemic state of the finances of universities should be remedied. The universities ought to be in a position to keep the best men available for training technical graduates in the method of research. The importance of research cannot be over-emphasised even from the point of view of industrial development. A person, who has spent a number of years in fundamental research is definitely better suited to take up an industrial career than a person who has specialised early in Industrial Chemistry. The good name of India will depend on the quality of research workers turned out by the universities and her industrial future will largely be determined by her ability to produce investigators of merit. It will not do to have confused ideas regarding the relative importance of fundamental knowledge and its practical application. Attempts to train personnel in the practical application of science against a background of an imperfect education in pure science can only give rise to people, who as my predecessor remarked, "will at the most be able to mend what we have but not build what we want."

Another serious handicap in our existing set up is the low status which a technical man generally occupies in Industry. Unless we safeguard security of tenure and adequate status of the technical man in Industry, we run grave risks.

The question of training research workers also raises the important question of medium of instruction. My predecessor, in his address at Allahabad, fully dwelt on this question at some length. It goes without saying that training and instructions, in order to be easily grasped, should be imparted in the mother tongue of the pupils. On the other hand, Science is international in character and has developed through the co-operative efforts of all lands. This co-operation occurs in the form of mental contacts and exchange of ideas. I fully agree with the conclusions, which my predecessor came to on this question. We shall have to depend on English in order to consult scientific literature and journals; we shall have to publish results of our investigations in English. Our present system of scientific education has been in vogue for nearly a century. Any radical change or transformation in it cannot be effected without arresting its progress for a while. Such a break will be disastrous when we are struggling to take our rightful place in the community of free nations.

With the partition of the country, the Food situation in India has become extremely acute. We have now to make large imports of foodgrains, which consume a very considerable portion of our foreign exchange resources. At present, in India, about 75% of the population is engaged in agricultural pursuits. We will now have to divert at least 25% of the population to the Industry, so that we can earn enough foreign exchange to pay for our large imports of capital goods. Uptil now we have

been largely depending on the exports of our minerals in order to earn necessary foreign exchange. India has supplied 40 million tons of high grade manganese ores since 1910 to the world at a price but little above the cost of mining and transport. Similarly, large exports of mica, chromite, magnesite, sillimanite and kyanite had to be maintained to procure foreign exchange. These resources are expendable resources and once we are depleted of these minerals, there will be no means of replacing these. The critical shortage in metals has been most seriously felt up to now only in respect of tin, zinc and lead. But signs are appearing that accessible deposits of copper, nickel, antimony in the world are diminishing. A policy of conservation will, therefore, have to be followed with respect to some of these minerals. If that is done, India will have to depend on her exports of industrial products for earning her foreign exchange. This can only be done by developing industries on a well-planned and co-ordinated basis. Scientific man-power, industrial raw materials and other natural resources will have to be rigidly planned. In this task, the Indian Chemical Society will naturally play an important role. It is imperative that our Society remains completely aloof from political influences and the members take a detached view of the national problems and are able to offer their advice in a most free and frank manner.

## SCHIFF'S BASES FROM DIAMINODIPHENYLSULPHONE

BY U. P. BASU AND K. R. CHANDRAN

Certain Schiff's bases of 4:4'-diaminodiphenylsulphone have been described.

4:4'-Diaminodiphenylsulphone is known to have powerful antibacterial properties, but it is somewhat toxic. Several compounds, disodium 4:4'-diaminodiphenylsulphone-N:N'-didextrose sulphonate, disodium 4:4'-diaminodiphenylsulphone-N:N'-diformaldehyde sulphoxylate and tetrasodium-4:4'-di- $\gamma$ -phenyl-*n*-propylaminodiphenylsulphone- $\alpha$ : $\gamma$ : $\alpha'$ : $\gamma'$ -tetrasulphonate, from its Schiff's bases have been prepared and are being found to be useful in the treatment of pulmonary tuberculosis and leprosy (cf. Brownlee, *Lancet*, 1948, ii, 131; Muir, *Trans. Roy. Soc. Trop. Med. & Hyg.*, 1948, 41, 575). Calloman and Raiziss (*Amer. Rev. Tuberc.*, 1946, 53, 374) have noticed certain advantages in the Schiff's base, disalicylidene derivative of 4:4'-diaminodiphenylsulphone against tuberculosis. As the researches of Smith *et al.* (*Proc. Soc. Exptl. Biol. Med.*, 1947, 64, 261) as well as that of Klotz (*J. Amer. Chem. Soc.*, 1944, 66, 459) tend to show that for biological reaction the drug should preferably contain one amino grouping, synthesis of Schiff's bases from 4:4'-diaminodiphenylsulphone with unsymmetrical groupings is being considered to be of interest. These derivatives may undergo fission in the system in a preferential way to give rise to a monoamino derivative to exert the characteristic drug action without exerting the toxic action of the diaminodiphenylsulphone.

It has already been noted by Buttle *et al.* (*Biochem. J.*, 1938, 32, 110) that 4:4'-diaminodiphenylsulphone does not generally form diarylidene derivatives by reacting with aromatic aldehydes.

Accordingly, 4:4'-diaminodiphenylsulphone has been reacted to form compounds of the type  $R.CH=N-C_6H_4.SO_2.C_6H_4.N=CH.R'$ , where R and R' are different groups. In the course of the investigations it has been noticed that the 4:4'-diaminodiphenylsulphone readily reacts with one molar amount of aromatic aldehyde and this mono-arylidene derivative of diaminodiphenylsulphone undergoes condensation easily with acetaldehyde and glucose. The cinnamic aldehyde behaves as an aliphatic aldehyde, and condenses readily with 4-benzylidene-, -anisylidene-, and -salicylidene-amino-4'-aminodiphenylsulphones when refluxed in alcoholic solution to afford the corresponding 4'-cinnamylidene-amino derivatives. (It itself also reacts with the sulphone to give the dicinnamylidene derivative, Buttle *et al.*, *loc. cit.*). Jain *et al.* (*Science & Culture*, 1946, 11, 567) have noticed that the two moles of aldehyde (aromatic) could not be condensed with one of 4:4'-diaminodiphenylsulphone. We have also noticed that a mono-salicylidene derivative could not be condensed with benzaldehyde or anisaldehyde under the usual conditions of reactions, nor when refluxed in presence of zinc chloride. But when it was refluxed with a fresh molar amount

of salicylaldehyde in alcoholic solution for over 4 hours, the disalicylidene derivative separated out in fine yellow-orange needles, m.p. 268-70°.

In the preparation of 4:4'-diaminodiphenylsulphone Raiziss's method (*J. Amer. Chem. Soc.*, 1939, **61**, 2763) was slightly modified and this has been described in the experimental part of the paper.

#### EXPERIMENTAL

The method is a slight modification of the procedure adopted by Raiziss *et al.* (*loc. cit.*). 4-Nitro-4'-acetylaminodiphenylsulphone was prepared according to the method of Raiziss *et al.* in their preparation of 4-amino-4'-hydroxydiphenylsulphone; but this was, however, simultaneously reduced and deacetylated by tin and hydrochloric acid to yield 4:4'-diaminodiphenylsulphone.

4-Nitro-4'-acetylaminodiphenylsulphone (90 g.) was suspended in a mixture of concentrated hydrochloric acid (675 c.c.) and water (270 c.c.) and heated to boiling. To this solution was added tin turnings (100 g.) from time to time, and after the addition was complete, the solution was heated for a further period of 2 hours. The mixture was treated with charcoal and filtered hot. The filtrate was cooled and basified with the addition of a concentrated solution of caustic soda (50%). The 4:4'-diaminodiphenylsulphone separated out on cooling as a crystalline, curdy precipitate and was purified by crystallisation from alcohol, m.p. 175°, yield 40 g.

*Preparation of 4-Arylidene-amino-4'-cinnamylidene-aminodiphenylsulphone.*—The 4-benzylidene-amino- and 4-p-methoxybenzylidene-amino-4'-aminodiphenylsulphones were prepared according to Buttle *et al.* (*loc. cit.*) and the 4-salicylidene-amino-4'-aminodiphenylsulphone was prepared by heating an alcoholic solution of 4:4'-diaminodiphenylsulphone with molar amount of salicylaldehyde for about 20 minutes. The mixture was cooled and the orange-yellow solid separating, was collected. This was washed with ether, and found to melt at 225-26°. Jain *et al.* (*loc. cit.*) recorded the melting point of this derivative as 172°.

All the above mono-arylidene derivatives were mixed with an alcoholic solution of cinnamic aldehyde (1.12 mole) and refluxed for 2 to 3 hours. The mixture was concentrated and diluted with ether. The diarylidene derivatives separated. These were filtered and washed with ether.

The 4'-amino group of the above 4-arylidene-amino-4'-aminodiphenylsulphone could not be condensed with benzaldehyde or anisaldehyde. But the same of salicylidene-amino derivative readily condensed with acetaldehyde, glucose, and even salicylaldehyde when heated under reflux in alcoholic solution as usual. In the case of glucose, a trace of ammonium chloride was added to bring about the reaction. From the ease of reaction it appeared that cinnamic aldehyde behaved as an aliphatic one and had been found to react easily with 4'-amino group of the 4-arylidene-amino-4'-aminodiphenylsulphones.

*Preparation of 4-Acetyl-amino-4'-arylidene-aminodiphenylsulphone.*—Although the monoarylidene-aminodiphenylsulphone did not react so readily with a second molecule

of an aromatic aldehyde, the 4-acetylamino-4'-aminodiphenylsulphone, however, reacted with cinnamic aldehyde as well as with salicylaldehyde when refluxed in alcoholic solution as usual.

The characteristics of the compounds are recorded in the table below.

TABLE I

General formula :  $R=N(4) \cdot C_6H_4SO_2 \cdot C_6H_4 N(4')=R'$ .

Compound		General appearance	Formula and Mol. Wt	Nitrogen %	
R=	R'=			Found.	calc
1. Salicylidene	H <sub>2</sub>	Yellow needles, m.p. 225-26°	C <sub>19</sub> H <sub>16</sub> O <sub>3</sub> N <sub>2</sub> S (352)	7.47	7.97
2. Salicylidene	Cinnamylidene	Yellow needles, m.p. 154-55°	C <sub>28</sub> H <sub>22</sub> O <sub>3</sub> N <sub>2</sub> S (466)	5.72	6.0
3. Benzylidene	Cinnamylidene	Yellow powder, m.p. 173-74°	C <sub>26</sub> H <sub>22</sub> O <sub>3</sub> N <sub>2</sub> S (450)	6.4	6.22
4. Anisylidene	Cinnamylidene	Yellow powder, m.p. 177-78°	C <sub>29</sub> H <sub>24</sub> O <sub>3</sub> N <sub>2</sub> S (480)	5.96	5.83
5. Salicylidene	Ethylidene	White needles, m.p. 162-63°	C <sub>21</sub> H <sub>18</sub> O <sub>3</sub> N <sub>2</sub> S (378)	7.42	7.41
6. Salicylidene	2:3:4:5:6-Penta-hydroxyhexylidene	White powder, m.p. 243-45°	C <sub>26</sub> H <sub>28</sub> O <sub>8</sub> N <sub>2</sub> S (514)	5.92	5.44
7. Acetyl	Cinnamylidene	Yellow needles, m.p. 219-20°	C <sub>23</sub> H <sub>20</sub> O <sub>3</sub> N <sub>2</sub> S (404)	6.95	6.93
8. Acetyl	Salicylidene	Orange crystals, m.p. 243-44°	C <sub>21</sub> H <sub>18</sub> O <sub>4</sub> N <sub>2</sub> S (394)	7.28	7.1

BENGAL IMMUNITY RESEARCH INSTITUTE,  
CALCUTTA.

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STUDIES IN THE NATURE OF HYDRATED FERRIC OXIDE. PART I.  
INFLUENCE OF TEMPERATURE AND CONCENTRATION ON  
THE NATURE OF THE PRECIPITATE OBTAINED BY THE  
INTERACTION OF SOLUTIONS OF FERRIC CHLORIDE  
AND SODIUM HYDROXIDE

BY ARUN K. DEY AND SATYESHWAR GHOSH

Ferric oxides of different physical properties and chemical character have been prepared for the first time by the precipitation from ferric chloride employing different quantities of sodium hydroxide and by carrying on the precipitation at different temperatures. The variation in the properties has been ascribed to the amphoteric nature of the oxide and a mechanism to explain the behaviour of ferric hydroxide has been suggested. The hypothesis has been supported by quantitative studies on the adsorption of the various ions in the system, during the precipitation of hydrated ferric oxide. The conductometric study of the precipitation has also been made.

Two varieties of ferric oxide are well known; Tommasi in 1882 (vide Weiser, "Hydrous Oxides", 1926, p. 364) recorded the existence of yellow and brown oxides, which were regarded by him as isomers. It was noted by Davies (*loc. cit.*) that the yellow variety, prepared by the oxidation of ferrous oxide or the carbonate, was denser and the solubility of this type of oxide in acids was very little. Weiser and Milligan (*J. Phys. Chem.*, 1935, **39**, 25; 1940, **44**, 1081) observe that the freshly precipitated oxide is amorphous, but on ageing it gradually transforms from  $\alpha\text{-Fe}_2\text{O}_3$  to  $\beta\text{-FeOOH}$ . The yellow  $\beta$ -oxide is also the product of the slow hydrolysis of ferric chloride (*J. Amer. Chem. Soc.*, 1935, **57**, 238). Thiessen and Köppen (*Z. anorg. Chem.*, 1930, **189**, 113; 1936, **228**, 57) opine that brown ferric oxide yields eight hydrates on isothermal dehydration, but their view has been challenged by Weiser and co-workers (*J. Phys. Chem.*, 1939, **43**, 1104). Not much work seems to have been done on the yellow oxide, and nothing is on record regarding the preparation of both of these oxides from the same reagents. It has, however, been observed by Banerji and Ghosh (*Nat. Acad. Sci., India*, Abstracts, 1942) that hydrated ferric oxide, when allowed to age gradually, becomes insoluble in mineral acids. They also observed remarkable variation in the peptisability of the oxide by hydrochloric and other acids with age. In the present investigation we have been able to prepare hydrated ferric oxides of varying colour beginning from deep brown to yellow by regulating the temperature and the concentrations of the reactants in the reaction between ferric chloride and sodium hydroxide solutions. We have also observed that in all the cases precipitation is complete even before the theoretical quantity of alkali is added. The same phenomenon has been recorded by Britton (*Ann. Rep.*, 1943, **40**, 44) who studied the precipitation of various oxides by the E. M. F. method. A similar observation has been made by Dey and Ghosh (this *Journal*, 1947, **24**, 181) during the study of the precipitation of cupric hydroxide from cupric sulphate solution when the quantity of alkali required was 14% less than the theoretical amount. We have in this study made a quantitative investigation of the precipitation of ferric hydroxide by analytical and conductometric methods.

## E X P E R I M E N T A L

A solution of AnalaR ferric chloride was prepared and both iron and chlorine were estimated volumetrically and gravimetrically and were in the proportion required by the formula  $\text{FeCl}_3$ . At the outset, to 10 c.c. of ferric chloride solution were added different quantities of a standard solution of sodium hydroxide (total volume 40 c.c.) and the quantity required for just complete precipitation was noted. After filtration the filtrate was tested and was found to be acidic when smaller volumes of alkali solution were employed. The volume of alkali solution needed to yield a just alkaline filtrate was also noted. The observations were repeated at several temperatures.

TABLE I

Ferric chloride soln. = 0.575M. Sodium hydroxide soln. = 1.9418M. Theoretically 10 c.c. of ferric chloride solution  $\equiv$  8.88 c.c. of alkali for precipitation of  $\text{Fe}(\text{OH})_3$ .

	Volume of NaOH solution at temperature of				
	25°.	40°.	50°.	60°.	80°.
For complete precipitation	8.30 c.c.	8.30 c.c.	8.50 c.c.	8.30 c.c.	8.30 c.c.
For a neutral filtrate	9.00	9.00	9.00	8.90	8.90

The effect of dilution was studied by diluting both the solutions of ferric chloride and sodium hydroxide ten times and similar observations were repeated; the results are shown in Table II.

TABLE II

Ferric chloride soln. = 0.0575M. Sodium hydroxide soln. = 0.1942M. Theoretically 10 c.c. of ferric chloride solution should require 8.88 c.c. of sodium hydroxide for precipitating  $\text{Fe}(\text{OH})_3$ .

	Volume of NaOH solution at temperature of		
	25°.	50°.	80°.
For complete precipitation	8.50 c.c.	8.60 c.c.	8.60 c.c.
For a neutral filtrate	9.10	9.00	8.90

We thus find that on dilution the precipitation value approximates the theoretical values, and on raising the temperature, the values undergo negligible change. It was further observed that the samples of solid precipitates were readily soluble in hydrochloric and nitric acids, when precipitated with alkalis less than the theoretical amounts. The colour of hydrated ferric oxide in all these cases were dark brown. When the amount of alkali was increased the precipitate became more and more insoluble in acids. When the alkali was in great excess, the precipitate became more yellow in colour and when 10 c.c. of alkali were employed for precipitation, the colour of the oxide was deep yellow and a fair portion of the precipitate remained undissolved in even hot and concentrated hydrochloric and nitric acids, leaving a yellow residue. This insolubility was more pronounced when the precipitation was carried out at higher temperatures.

Now to 10 c.c. of ferric chloride solution, taken in several 100 c.c. flasks kept at constant temperature, were added different volumes of alkali solution, total volume

was raised to 100 c.c. and they were maintained at constant temperature for an hour. The amount of iron, sodium and chlorine ions, and also hydrogen or hydroxyl ions in the supernatant liquid were determined accurately using a microburette, by the usual methods. Knowing the amounts of the different ions taken, the amounts of ions associated with the precipitate were calculated. The results obtained at different temperatures are recorded in the following tables.

Ferric chloride solution = 0.575M

NaOH solution = 1.9418M

Iron = 0.575 g. ions per litre

Hydroxyl = 1.9418 g. ions per litre

Chlorine = 1.725 g. ions per litre

Sodium = 1.9418 g. ions per liter

TABLE III

Temperature = 25°

Mg. ions taken.			Mg. ions available in supernatant liquid.			Mg. ions associated with ppt.		
Fe.	Cl.	NaOH.	H or OH.	Cl.	Na.	Fe.	Na.	Cl.
5.75	17.25	14.56	1.84 H	6.76	—	2.15	—	10.49
5.75	17.25	15.53	0.76	5.14	—	2.00	—	12.11
5.75	17.25	16.12	0.45	15.17	16.12	Nil	Nil	1.78
5.75	17.25	16.89	0.05	15.95	16.77	„	0.12	1.30
5.75	17.25	17.28	0.07 OH	16.49	17.14	„	0.14	0.76
5.75	17.25	19.42	1.67	17.24	19.17	„	0.25	0.01

TABLE IV

Temperature = 50°.

Mg. ions taken.			Mg. ions available in supernatant liquid.			Mg. ions associated with ppt.		
Fe.	Cl.	NaOH.	H or OH.	Cl.	Na.	Fe.	Na.	Cl.
5.75	17.25	15.53	0.665 H	11.01	—	4.05	—	6.21
5.75	17.25	16.12	0.041	15.29	16.12	Nil	Nil	1.96
5.75	17.25	16.50	0.016	16.64	16.50	„	„	0.61
5.75	17.25	16.89	0.010	16.88	16.77	„	0.12	0.39
5.75	17.25	17.28	0.078 OH	17.10	17.12	„	0.16	0.15
5.75	17.25	19.42	1.598	17.13	19.04	„	0.38	0.12

TABLE V

Temperature = 80°.

Mg. ions taken.			Mg. ions available in supernatant liquid.			Mg. ions associated with ppt.		
Na.	Cl.	NaOH.	H or OH.	Cl.	Na.	Fe.	Na.	Cl.
5.75	17.25	15.53	0.700 H	15.45	—	0.90	—	1.80
5.75	17.25	16.12	0.214	15.09	16.12	Nil	Nil	1.16
5.75	17.25	16.50	0.011	13.89	16.50	„	„	3.36
5.75	17.25	16.89	0.009	14.07	16.75	„	0.14	3.18
5.75	17.25	17.28	0.074 OH	15.76	17.11	„	0.17	1.49
5.75	17.25	19.42	1.760	16.10	18.64	„	0.78	1.15

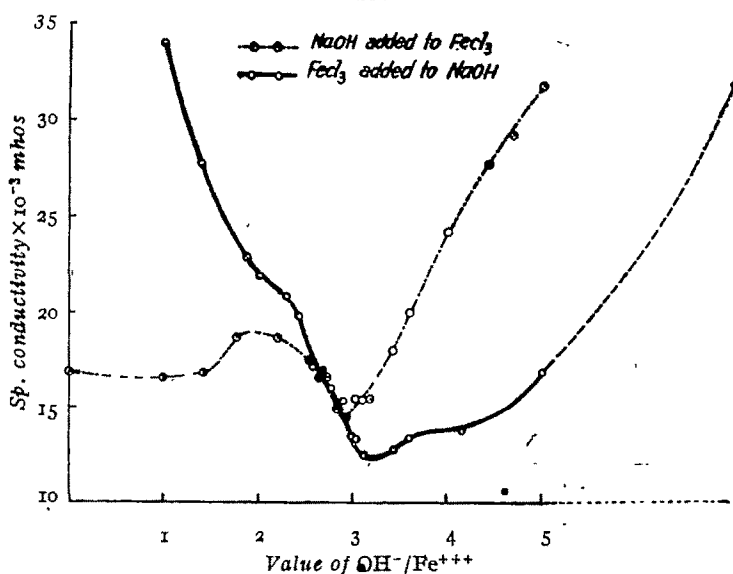
The precipitation was also studied by noting the electrical conductivities of the supernatant liquid in the different cases when varying proportions of ferric and alkali solutions were used. For conductometric measurements a great accuracy and precision was maintained. Instead of the cell constant, the calibration constant at different positions of the bridge wire was determined by the method of Wark (*J. Phys. Chem.*, 1930, **34**, 885), and these values were employed for the calculations.

To 5 c.c. of  $M/10$  ferric chloride solution were added different volumes of  $M/2$  sodium hydroxide solution, total volume kept at 10 c.c. and the precipitate allowed to settle for an hour at  $30^\circ$ . It was centrifuged at 2500 r.p.m. for five minutes and the electrical conductivity of the supernatant liquid was determined at  $30^\circ$ .

In another set, the concentration of alkali was kept constant and varying amounts of ferric chloride solution were added to it. The concentration chosen was  $M/4$  for both the reactants, so that at the equivalence point  $\text{Fe} : \text{OH} = 1 : 3$ , the concentration of the respective constituents in both the sets was almost the same.

From the conductivity results the adjoining graph has been plotted showing the variation of specific conductivity with the increase in  $\text{Fe} : \text{OH}$  ratio (Fig. 1).

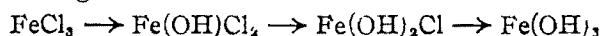
FIG. 1



#### DISCUSSION

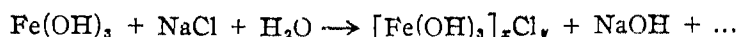
Our results on the precipitation of hydrated ferric oxide from ferric chloride solution show that similar to the observation of Britton (*Ann. Rep.*, 1943, **40**, 43) with various hydroxides, the amount of alkali needed for complete removal of the metal from solution is always less than the theoretical amount. In all such cases there are two possible reactions, which would result to such an observation.

(1) Increased tendency of hydrolysis with increased concentration of the alkali, according to the following scheme :



The above will be more marked with increasing insolubility of the respective hydroxides and their strength as a base.

(2) Hydrolytic adsorption of the anion, Cl- by the basic oxide, producing free alkali :



In the first case the formation of ferric hydroxide takes place in stages, yielding various intermediate basic compounds, which ultimately with a definite excess of alkali would result in the formation of  $\text{Fe}(\text{OH})_3$ . In the second case, the quantity of alkali added precipitates the equivalent quantity of ferric hydroxide, which on adsorbing chlorine ions from the system liberates an equivalent quantity of  $\text{OH}^-$  ions, which precipitate more and more of the hydroxide. Our experimental results, as recorded in Tables III, IV and V, show that when the amount of alkali is deficient, the adsorption of chloride ion is high and this goes on decreasing as the quantity of alkali added is raised.

It is interesting to observe in Tables I and II that complete precipitation occurs when the supernatant liquid is slightly acidic. We find that in all the cases quoted in the aforesaid tables, the amount of alkali needed to yield a neutral filtrate is always greater than the volume needed for complete precipitation. This observation is contradictory to the case of precipitation of cupric hydroxide as observed by us (*loc. cit.*), where the filtrate becomes alkaline with complete precipitation. It may therefore appear to be anomalous, but keeping in view that ferric hydroxide is far more insoluble than cupric hydroxide, complete precipitation occurs at a lower  $\text{OH}^-$  ion concentration, so that the filtrate may remain slightly acidic even though complete precipitation has been effected.

If we regard the precipitate to be a basic salt in accordance to equation (1), shown above, it is obvious that earlier precipitation should be favoured by dilution and also by rise of temperature, as both of these are favourable for hydrolysis. A perusal of Table I shows that the amount of alkali needed for complete precipitation is not markedly affected by rise of temperature. From Table II it will be seen that with dilution precipitation occurs with the amount of alkali approaching theoretical values.

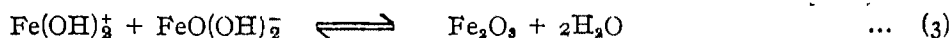
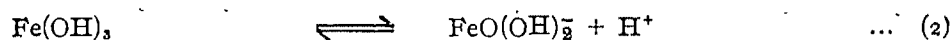
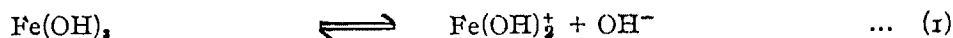
Considering the analytical data for adsorption, as presented in Tables III, IV and V, we find that the adsorption of sodium and chlorine ions varies remarkably with the amount of alkali used for precipitation. The adsorption of chlorine in general decreases, whilst the amount of sodium associated with the precipitate increases with increasing quantities of alkali added. These observations are easily explainable, when we remember that ferric oxide has an amphoteric character and the tendency of the adsorption of ions by such oxides is always governed by the hydrogen ion concentration of the medium in which the adsorption is taking place (Dey and Ghosh, *Proc. Nat. Acad. Sci., India*, 1946, 16A, 143). Naturally when the  $\text{OH}^-$  ion concentration is low, the adsorption of  $\text{Cl}^-$  ions will be more prominent, while under such circumstances  $\text{Na}^+$  ions will not be adsorbed. Thus, we find that at  $25^\circ$  (vide Table III) when the medium is prominently acidic containing 0.45 mg. *M* of acid, the adsorption of chlorine is 1.78 mg. ions, whereas the adsorption of sodium is nil. Now, as the medium becomes alkaline,

containing 1.67 mg. *M* of alkali, the adsorption of chlorine falls to 0.01 mg. ions, whereas the amount of sodium associated is 0.25 mg. ions.

Increase of temperature favours the association of sodium with the precipitate, whereas the adsorption of chlorine is diminished. The latter is, however, not rigidly followed by changes in temperature, as the phenomenon of hydrolysis at higher temperatures plays an important role. The association of sodium ions with the precipitate goes on increasing steadily with rise of temperature. Thus, when 19.42 mg. *M* of alkali are added to ferric chloride solution containing 5.75 mg. ions of ferric iron, the amount of sodium associated with the precipitate is 0.25, 0.38 and 0.78 mg. ions at 25°, 50° and 80° respectively.

Ferric oxide with sodium hydroxide has a tendency to form sodium ferrite, and this will naturally be more prominent at a high temperature. Van Benmelen in 1892 (vide Weiser, "Hydrous Oxides") prepared the yellow variety of ferric oxide by the reaction between sodium ferrite and water. We are of opinion that at higher temperatures sodium is found to be associated in larger amounts in alkaline media, as direct chemical interaction results to form some sodium ferrite.

It is interesting to point out that ferric hydroxide, obtained at higher temperature with excess of alkali, was definitely found to be of yellow colour and was highly resistant towards acids. This confirms our contention that a fair portion of the ferric hydroxide undergoes a chemical transformation to form ferric ferrite, which has lost its basic properties to be acted upon by an acid, according to the following scheme :



In equation (1) ferric hydroxide acts as a proton acceptor, *i. e.* as a base and in equation (2) it donates a proton, and behaves as an acid. The chemical interaction between the acidic and the basic properties of the hydroxide in the above manner results in the formation of  $\text{Fe}_2\text{O}_3$ , which becomes chemically inert either as an acid or a base.

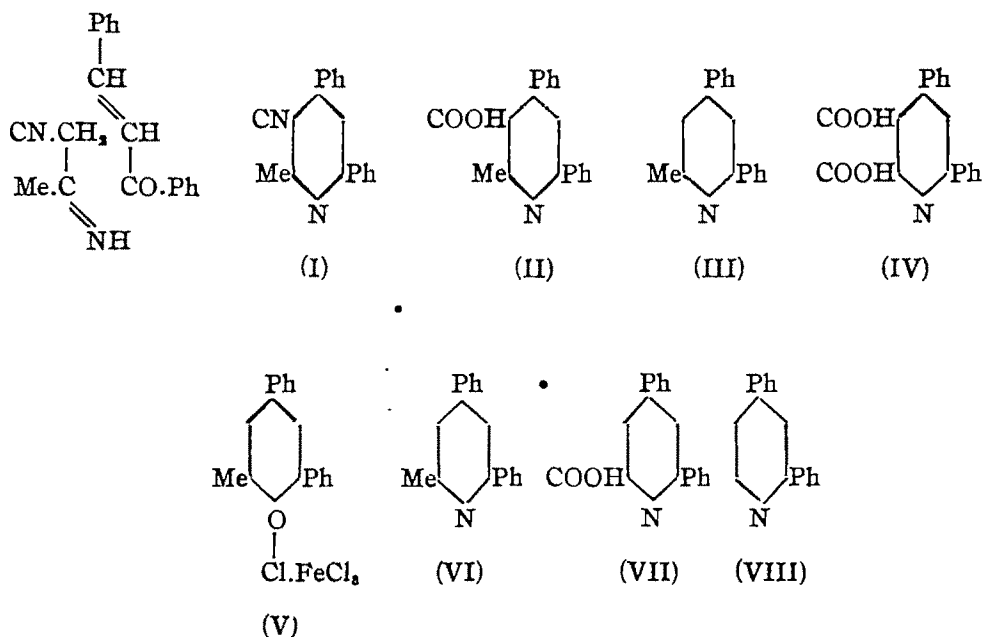
The conductometric study of the precipitation of ferric hydroxide shows that though complete precipitation of iron as hydrated oxide takes place with a little lesser amount of alkali, yet the minima of the conductometric graph occurs, when Fe : OH ratio is 1 : 3.2 when ferric chloride is added to the alkali, whilst it is 2.9 when alkali is added to ferric chloride. In neither case the minima correspond to the observed ratio for complete precipitation. We are of opinion that this divergency of the results occurs due to the adsorption of the electrolytes present, and hence no accurate information can be obtained regarding the complete precipitation from these curves. We therefore suggest that Britton's data on the precipitation of different insoluble hydroxides using the E. M. F. method (*loc. cit.*) is also beset with similar difficulties and hence fails to convey a true idea of the conditions of precipitation.

# MEYER'S SYNTHESIS OF PYRIDINES FROM AMINOACRYLO- NITRILES : VERIFICATION IN THE LIGHT OF GASTALDI'S OBJECTIONS

BY NIRMALANANDA PALIT

The reactions of dinitriles have been extensively studied by V. Meyer and have proved to be a fruitful source for the preparation of pyridines. A typical member of the series has been obtained by Gastaldi from the corresponding pyrilium salt and has been found to be different. This questions the correctness of the structure of Meyer's compounds. In the present investigation it has been shown that the structures of Meyer's compounds as a class are not incorrect, but so far as the particular member is concerned, Gastaldi's contention probably holds good and Meyer's compound may have to be represented differently.

Meyer has developed a method for the synthesis of pyridines.  $\beta$ -Amino- $\beta$ -methylacrylonitrile was condensed with benzylidene-acetophenone in presence of sodium ethoxide to yield 3-cyano-2:4-diphenyl-6-methylpyridine (I). The cyano group was hydrolysed with concentrated HCl at  $260^\circ$  to the carboxy derivative (II) which, when heated with lime, lost carbon dioxide and gave 2:4-diphenyl-6-methylpyridine (III), m.p.  $156^\circ$ . The compound (II) on oxidation with permanganate gave 2:4-diphenylpyridine-5:6-dicarboxylic acid (IV), m.p.  $185^\circ$  (V. Meyer and Irmscher, *Chem. Zentr.*, 1908, II, 594).



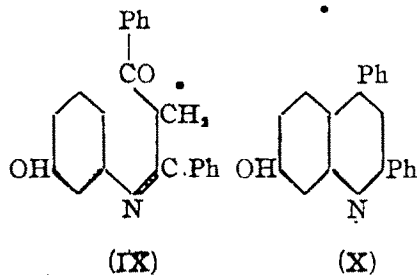
Gastaldi has thrown considerable doubt on this reaction. He has obtained (VI) from acetophenone or dypnone by the action of acetic anhydride in presence of ferric

chloride and treating the resulting pyrilium salt (V) with ammonia and found it to be different from (III), m.p.  $73^{\circ}$ . Oxidation of (VI) with permanganate in 5% sulphuric acid gave an acid (VII), the sodium salt of which on heating with lime at  $400^{\circ}$  formed 2:4-diphenylpyridine (VIII) (cf. *Chem. Zentr.*, 1922, III, 778 ; 1923, I, 759).

The author while studying a reaction, similar to that of Meyer (*this Journal*, 1937, 14, 355), obtained products which were assigned structures based on certain experiments which definitely proved the constitution of the dicarboxypyridine compound (IV) and indicated that Meyer's mode of representing the reaction as a class is not incorrect. Those experiments form the subject matter of the present communication.

In the light of Gastaldi's research it became necessary to investigate Meyer's reaction more critically and for this purpose, in the first instance, the reaction was slightly modified in such a way that any chance of ambiguity was very much restricted. Thus,  $\beta$ -amino- $\beta$ -phenylacrylonitrile was condensed with *O*-ethyl ether of dibenzoylmethane, a substance which can hardly be expected to react in any abnormal way. The product formed was identical with 3-cyano-*sym*-triphenylpyridine, obtained by Meyer from the same aminonitrile and benzylidene acetophenone (*loc. cit.*). This reaction can scarcely be regarded as capable of taking any other course. Moreover, this cyanopyridine derivative on hydrolysis lost carbon dioxide and gave *sym*-triphenylpyridine, identical with that previously obtained by Newman from the monoxime of benzaldiacetophenone by passing dry HCl in benzene solution (*Annalen*, 1898, 302, 240). This identity with Newman's compound, formed by an entirely different method, lends support to the correctness of Meyer's compounds.

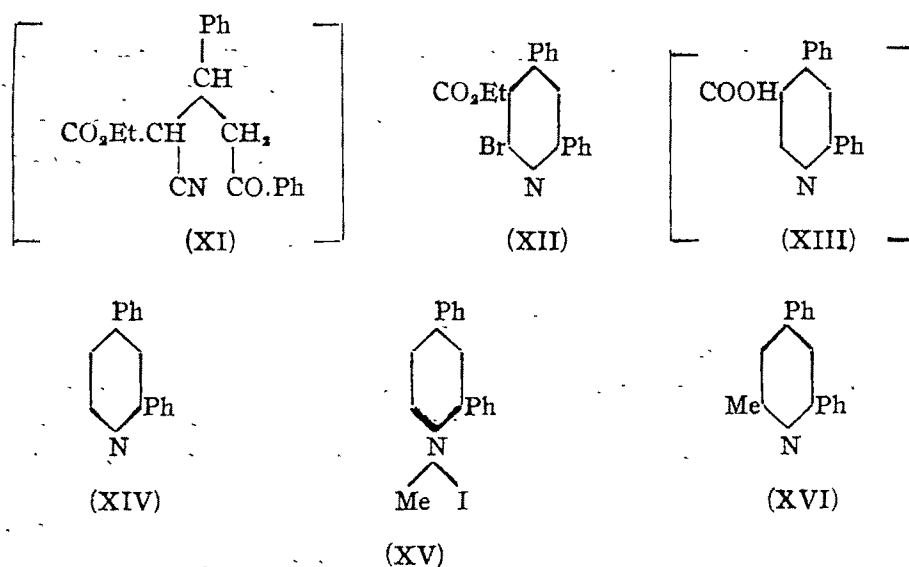
In the second instance, (IV) has also been obtained by an equally different method. Dibenzoylmethane reacts with *m*-amidophenol to form an anil (IX) which with dry HCl in glacial acetic acid solution closes up the ring to form 2:4-diphenyl-7-oxyquinoline (X) (Bulow and Issler, *Ber.*, 1903, 36, 4017). It has now been obtained more conveniently by boiling *m*-amidophenol and benzylidene-acetophenone in alcoholic solution with a trace of alkali as the condensing agent. Permanganate oxidises the oxyquinoline to give 2:4-diphenylpyridine-5:6-dicarboxylic acid, identical with Meyer's compound (IV).



These evidences therefore establish the fact that Meyer's reaction is generally correct, and if there is any doubt, it must be with the individual member (III), and to settle this issue it was thought desirable to synthesise it in such a way as would definitely prove its constitution. Ethyl  $\beta$ -aminocrotonate, which reacts with ethyl acetylpyruvate-



vigorously even at  $0^{\circ}$  (Mumm and Hüneke, *Ber.*, 1917, **50**, 1568), failed to react with dibenzoylmethane with alkaline condensing agents or when heated with zinc chloride under suction. The 1:5-diketone from styrylphenyl ketone and acetoacetic ester (Knoevenagel, *ibid.*, 1902, **35**, 397) when treated with ammonia suffers intramolecular ring-closure before it can react with the latter. Next the synthesis was attempted from dypnone and acetamide by heating them together with zinc chloride in a sealed tube at  $340^{\circ}$  for 48 hours according to the method of Pictet and Stchelin (*Compt. rend.*, 1916, **162**, 876) but the analysis of the products did not agree with the pyridine in question. The following scheme was more successful.



Using methyl cyanoacetate the course of the above reaction was followed up to the bromo-ester corresponding to (XII) by Kohler, Graustein and Merrill (*J. Amer. Chem. Soc.*, 1922, **44**, 2536). With the more common ethyl ester, it was noticed that the formation of (XI) did not proceed to completion unless the mixture was maintained just alkaline throughout the reaction by occasional additions of drops of sodium methoxide solution. Bromine in glacial acetic acid converted the open-chain nitrile into the bromopyridine derivative (XII). This was reduced with HI and the product obtained (XIII) on dry distillation with excess of barium hydroxide lost carbon dioxide and gave 2:4-diphenylpyridine, identical with Gastaldi's compound (VIII). This energetically combined with methyl iodide on a water-bath and the methiodide at  $300^{\circ}$  (Ladenburg, *Ber.*, 1883, **16**, 1410, 2059; Lange, *ibid.*, 1885, **18**, 3438; Koenigs and Hoffmann, *ibid.*, 1915, **58**, 194) formed a mixture the major component of which was diphenylpyridine, but it also contained (V, m.p.  $73^{\circ}$ ) which was identified by its picrate. Meyer's compound (III, m.p.  $156^{\circ}$ ) was not formed. The very small amount of material at hand and the unsatisfactory yields obtained by this process precluded any further study here and the work has been taken up again with a different line of approach which will be duly communicated.

## E X P E R I M E N T A L

3-Cyano-2:4:6-triphenylpyridine (I, Ph in place of Me).— $\beta$ -Amino- $\beta$ -phenylacrylonitrile (2.8 g.) (Holtzworth, *J. prakt. Chem.*, 1889, ii, 39, 242) and dibenzoylmethane-O-ethyl ether (5 g.) (Ruheman and Watson, *J. Chem. Soc.*, 1904, 88, 462) were dissolved in absolute alcohol and introduced into alcoholic sodium ethoxide (Na, 0.46 g.). The liquid immediately assumed a deep red tint. Within half an hour it set to a semi-solid mass. Next day it was filtered at the pump and repeatedly washed with alcohol till perfectly white, yield 2 g. It was crystallised from a large volume of alcohol, m.p. 220° (Meyer, m.p. 220°). (Found: C, 86.4; H, 5.2; N, 8.5.  $C_{24}H_{16}N_2$  requires C, 86.7; H, 4.8; N, 8.4 per cent).

*Hydrolysis: sym-Triphenylpyridine.*—The hydrolysis was effected by heating the cyano compound with fuming HCl in a sealed tube at 260° for 4 hours. On adding water a flocculent white precipitate was obtained which did not dissolve in NaOH solution. It crystallises in needles from ethyl acetate, acetone, alcohol and is least soluble in the last, m.p. 136-37° (Found: N, 4.7.  $C_{23}H_{17}N$  requires N, 4.56 per cent). A mixed melting point determination with the compound obtained by Newman's method showed no depression.

7-Hydroxy-2:4-diphenylquinoline (X).—*m*-Amidophenol (2.5 g.) and styrylphenyl ketone (5 g.) were dissolved in absolute alcohol (40 c.c.) and boiled under reflux for 7 hours with the addition of a few drops of alcoholic potash. The solution turned red and on cooling set to a crystalline mass. This was collected and crystallised from benzene, yield 2 g. Unlike the crude product it no longer tarnished in air and light, m.p. 273° (turns brown). The alcoholic mother-liquor on concentration gave a further yield of 1 g. (Found: C, 85.21; H, 5.23; N, 4.67.  $C_{21}H_{15}ON$  requires C, 84.84; H, 5.05; N, 4.71 per cent). Picrate, shining orange-yellow flakes, m.p. 246-47°. (Found: N, 10.8.  $C_{21}H_{15}NO.C_6H_3O_7N_3$  requires N, 10.6 per cent).

*Oxidation of the Quinoline Compound: 2:4-Diphenyl-5:6-dicarboxylic Acid (IV).*—The oxyquinoline derivative (3 g.) was dissolved in aqueous KOH (conc., 3 g. excess was used to prevent hydrolysis on dilution) and then diluted with warm water to 450 c.c. The solution was heated on a water-bath. 5%  $KMnO_4$  (Tech., 9 g.) was very slowly added to it with stirring till the mixture became permanently pink; excess of  $KMnO_4$  was decomposed with  $SO_2$ , filtered hot, and the precipitated oxide extracted with hot water. The filtrate was concentrated with occasional neutralisation with dilute  $H_2SO_4$  to a small bulk when copious gelatinous inorganic matter separated. This was filtered off and the filtrate with copper sulphate solution precipitated a greenish blue copper derivative which was collected, washed, suspended in water and decomposed with  $H_2S$ . The gummy precipitate was extracted with warm dilute caustic soda and acidified, when a spongy mass was produced. The whole thing was extracted with ether, dried with calcium chloride and the solvent evaporated. The residue was crystallised from absolute alcohol, m.p. 185° (gas evolution), yield too poor. (Found: C, 71.2; H, 4.4; N, 4.7.  $C_{19}H_{13}O_4N$  requires C, 71.5; H, 4.1; N, 4.4 per cent).

*Condensation of Ethyl Cyanoacetate with Benzylidene-acetophenone (XI).*—The condensation did not proceed satisfactorily unless very pure chemicals were used in absolutely dry condition. The ketone (20 g.) and the ester (14 g.) were dissolved in carefully dehydrated methyl alcohol (30 g.) and to the warm solution sodium methoxide (5% soln.) was added dropwise till distinctly alkaline. The temperature of the reaction mixture shot up and the liquid began to boil. It was then refluxed for 2 hours with repeated additions of the condensing agent (2 drops, each time) to keep it alkaline throughout. After standing overnight the solvent was removed, the residue taken up in ether, washed with sodium carbonate, dried ( $\text{CaCl}_2$ ) and finally distilled. At 10 mm. pressure a few drops of cyano-ester passed off below  $100^\circ$  and then the temperature began to rise till at  $200^\circ$  tendency to decomposition was noticed. It was a very thick, viscous, transparent mass not solidifying even on keeping in ice for several days nor could it be crystallised from any solvent, yield 28 g.

*Action of HBr on above Open-chain Addition Product : Formation of Ethyl 2-Keto-4:6-diphenyltetrahydropyridine-3-carboxylate.*—The above light brown mass was dissolved in warm carbon tetrachloride and saturated with dry HBr. The solution on keeping in an ice chest solidified completely. On rubbing with methyl alcohol shining white flakes were obtained, m.p.  $150-55^\circ$ , yield 22 g. It was crystallised from alcohol, m.p.  $160^\circ$ . (Found : C, 74.3 ; H, 6.1 ; N, 4.7.  $\text{C}_{20}\text{H}_{19}\text{O}_3\text{N}$  requires C, 74.76 ; H, 5.91 ; N, 4.4 per cent). Hydrolysis of this ester gave the acid identical with Kohler's product (*loc. cit.*).

*Action of Bromine : Formation of Ethyl 2-Bromo-4:6-diphenylpyridine-3-carboxylate (XII).*—The open-chain compound (XI) was treated with bromine in hot glacial acetic acid. Copious HBr was evolved and towards the end a very slight white granular precipitate appeared which was identified to be ammonium bromide, suggesting hydrolysis of a part of the material. This was filtered off, the filtrate distilled under suction and the acid fumes removed in a vacuum desiccator over solid KOH. The residual thick brownish mass was boiled with water when it became nearly semi-solid but separated from solvents as an oil. The mass was next treated with hot caustic soda solution which dissolved a considerable portion of it to form a red solution from which a quantity of the ketotetrahydropyridine ester, described above, was recovered. The residue was a hard, red, impure solid which was repeatedly crystallised from alcohol with the addition of animal charcoal and kieselghur as oblong plates, m.p.  $133-35^\circ$ , yield very poor. (Found : Br, 20.97.  $\text{C}_{20}\text{H}_{16}\text{O}_2\text{NBr}$  requires Br, 20.94 per cent).

*Reduction of the Bromopyridine Ester.*—The bromo-ester (XII, 5 g.) was mixed with red phosphorus (1 g.) and hydriodic acid ( $d$  1.94, 12 c.c.) and heated in a sealed tube at  $175-180^\circ$  for 24 hours. With the disappearance of iodine vapours a colorless liquid with large crystals were obtained. The crystals turned violet on exposure to air and were soluble in warm water. These were treated with boiling potash solution and concentrated. On cooling the potassium salt separated as a rose-red solid, freely soluble in water. Acidification precipitated the acid (XIII) in an impure condition, m.p.  $200-205^\circ$ . The crude reduction product was refluxed with powdered barium hydroxide and a little water for 2 hours, cooled, filtered and dried.

*Removal of the Carboxyl group: Formation of 2:4-Diphenylpyridine (XIV).—*The dry material was well mixed with a little more barium hydroxide and heated gently with a small free flame in a pyrex test tube fitted with a delivery tube dipping in cold water. Decomposition started with frothing and very soon an oily distillate condensed on the cooler parts of the test tube. This solidified to a pale brown solid, yield 0.5 g. from 1 g. of the crude crystals obtained in the previous operation, m.p. 68° (pure) (Gastaldi, *loc. cit.*, m.p. 69°). (Found: N, 6.2.  $C_{17}H_{13}N$  requires N, 6.0 per cent). Picric acid in alcohol produced a deep yellow picrate, m.p. 189° (Gastaldi, m.p. 187°).

*2:4-Diphenylpyridine Methiodide (XV).—*This pyridine (1 g.) and methyl iodide (1.5 g.) were refluxed on a carbon lamp. Within an hour a red paste was formed which set to a glassy red solid on cooling. This was rubbed with warm rectified spirit when a yellow solid separated, m.p. 206-208°. It was recrystallised from alcohol, m.p. 210°. (Found: I, 34.1.  $C_{18}H_{16}NI$  requires I, 34.0 per cent).

*2:4-Diphenyl-6-methylpyridine.*—The methiodide (4 g.) was heated in a sealed tube at 300°-315° for 2 hours affording a black transparent soft mass which was taken up in hot water, treated with concentrated NaOH solution and distilled in steam. A slightly milky liquid passed over. Extraction of the distillate with ether, followed by removal of the solvent, gave a yellow oil having a strong odour of essential oil, but on keeping this volatile portion passed away leaving a very small amount brown solid which formed a picrate, m.p. 184-87°. This was probably diphenylpyridine.

The residue after steam-distillation was mixed with enough ether. Most of the black mass went into solution having a deep brownish green fluorescence. This was separated, filtered from the slight brown precipitate formed, solvent removed and the residue crystallised from ligroin. Impure crystals separated melting at about 60°, which energetically formed picrate. This was again mostly diphenylpyridine as the recrystallised picrate melted sharply at 169°. The mother-liquor (ligroin) was evaporated off, residue taken up in a little benzene, a few drops of petrol added and allowed to concentrate in air. Some crystals separated which were removed and washed with a little petrol. These melted at 69-72° and formed a picrate melting at 212°. The exceedingly poor yield of this compound and its admixture with diphenylpyridine, which is so close to it both in solubility in different solvents and melting point, indicated the unsuitability of this method.

## CHEMICAL EXAMINATION OF THE WOOD OF *CEDRELA TOONA*, ROXB. ISOLATION OF A LACTONE, AN ESSENTIAL OIL, AND A COLOURING MATTER

BY DHARAM BAL PARIHAR AND SIKHIBHUSHAN DUTT

From the wood of *Cedrela toona*, a lactone (m.p. 204°), an essential oil, and a colouring matter (m.p. 256°) have been obtained in yields of 0.40, 0.17 and 0.25% respectively

The lactone, Cedrelone, has a molecular formula  $C_{25}H_{38}O_5$ . It contains one ethylenic double bond, one phenolic hydroxyl, one ketonic group and a lactone ring in the molecule.

Several derivatives of Cedrelone have been prepared and analysed

*Cedrela toona*, commonly known as *Tun* in Hindi, is a tall handsome tree, about 50 to 60 feet high, belonging to the natural order of Meliaceae. It is found in abundance in the sub-Himalayan tract from the Indus eastwards, Chittagong, Assam, Burma, Chota Nagpur, Western Ghats of Bombay to the Nilgris and other hills of the Indian Peninsula.

The wood, which is of a brownish red colour, has a faintly aromatic odour, mainly due to the presence of a golden yellow essential oil, and a lactone. The wood is very light and is largely used in making light furniture and musical instruments. Mell (*Text. Col.*, 1931, 53, 68) found the wood to be an interesting source of a natural dyestuff.

Besides the commercial aspects, the plant enjoys a great repute in medicine. The bark of the plant is a powerful astringent and has been used with success in chronic infantile dysentery, and as a local astringent application in various forms of ulcerations (Kirtikar and Basu, "Indian Medicinal Plants", Vol. I, pp. 562-564). The infusion of the bark is given in intermittant fevers and blood complaints in Indo-China. The seeds have similar therapeutic value. The flowers are considered emmenagogue in Bombay, and are given in disordered menstruation.

The essential oil from the wood was analysed by Pillai and Sanjiva Rao (*J. Soc. Chem. Ind.*, 1931, 50, 220r). By steam-distillation of the powdered wood a golden yellow pleasant smelling essential oil (yield 0.44%) was obtained. The oil was found to consist of a tricyclic sesquiterpene, *l*-copaene (35%), and bicyclic hydrocarbons identified as cadinene. The sesquiterpene alcohol fraction consisted mainly of *l*-cadinol (13 %).

Apart from the essential oil, no systematic work on the wood of the plant has been done by any previous worker, and in view of the great medicinal importance of the plant, the present work was undertaken to find out the active principles present and to study their constitutions.

The authors while working on the wood of the plant have isolated a pleasant smelling, heavy, essential oil, a reddish yellow colouring matter (m.p. 256°) and a lactone (m.p. 204°), in yields of 0.17%, 0.25% and 0.40% respectively on the dry wood. The systematic chemical examination of the essential oil and the colouring matter will be

the subject of separate communications; while in the present one the lactone has been studied in detail.

The lactone, which has been named as "Cedrelone" by the authors, crystallises in colorless, glistening, rhombic needles and large hexagonal plates from benzene, melting sharply at  $204^{\circ}$ . It has a molecular formula of  $C_{25}H_{30}O_6$ , and contains one ethylenic double bond, one phenolic hydroxyl and one ketonic groups. Several derivatives of the compound were prepared and analysed and are described in the experimental part of the paper.

#### EXPERIMENTAL

For preliminary examination the powdered dry wood (25 g.) was taken in a Soxhlet's apparatus and extracted with different solvents in the hot each time, for about an hour and the solvent distilled off. The following are the percentages of the extracts obtained in each case:

Water	7.47 %	$CHCl_3$	1.49 %
MeOH	17.96	$CCl_4$	1.08
EtOH	11.74	Benzene	1.18
Acetone	8.90	Ether	1.38
Ethyl acetate	6.06	Petrol ether	1.09

The wood on complete ignition left 2.55% of a white ash.

The air-dried, powdered wood of the plant (10.2 kg.) was extracted with hot benzene under reflux in lots of 2 kilos at a time. The extracts were filtered hot, the solvent distilled off and the viscous reddish concentrate was allowed to stand for one week, when large colorless crystals settled down. These were filtered off through a Buchner funnel and rapidly washed with ether. The mother-liquor and the washings were collected. These on concentration gave three more crops of the same crystalline compound with identical melting points. The ultimate mother-liquor was completely freed from benzene by heating on a water-bath under reduced pressure in an atmosphere of carbon dioxide, thus affording a very thick red coloured oily stuff, which was found to be the solution of the lactone in essential oil. This was treated with alcoholic potassium hydroxide on the water-bath, excess of alcohol distilled off, the mixture after cooling diluted with water, and extracted with ether. The ethereal extract on recovery of the solvent gave a heavy, pleasant smelling essential oil (yield, 0.17 %). The alkaline solution on acidification with dilute hydrochloric acid precipitated the lactone, which had the same melting point as that of the original lactone, confirmed by mixed melting point when no change was noticed. The systematic work on the essential oil will be the matter of a separate communication.

The wood after extraction with benzene was further extracted with hot alcohol under reflux and the solvent distilled off when a syrupy residue was obtained. After removal of traces of the solvent by evaporation on the water-bath, the residue was extracted with hot acetone, the extract concentrated and the colouring matter precipitated with chloroform. The compound on drying was found to shrink at  $215^{\circ}$  and

melt at 254-56°. This was recrystallised from boiling glacial acetic acid in reddish yellow needles melting at 256°. On further crystallisations the melting point of the compound did not rise. Thus, 25.5 g. of the colouring matter were obtained in an yield of 0.25% on the weight of the dry wood. The colouring matter is soluble in water, alcohol, ethyl acetate and acetone, but insoluble in chloroform, petroleum ether and benzene. It dissolves in alcoholic KOH with a yellow coloration and turns red with concentrated sulphuric acid. To alcoholic ferric chloride it imparts a greenish brown coloration and with an alcoholic solution of lead acetate, a yellow precipitate is produced. Ordinarily it has got no action on Fehling's solution but only reduces it after hydrolysis, thus showing it to be a glucoside. On reduction with magnesium and methyl alcoholic hydrochloric acid it turns red, thus indicating the presence of a pyrone nucleus in the molecule. It was found to contain no methoxy groups.

The various crops of the colorless crystalline matter, mentioned above, were mixed together and recrystallised from the least amount of hot benzene after treatment with animal charcoal when the compound was obtained in fine, colorless, rhombic needles and hexagonal plates melting sharply at 204°, which even after repeated crystallisation of the compound did not rise any further. Thus, 41 g. of the crystalline compound were obtained in an yield of 0.40% on the weight of the dried wood.

Cedrelone possesses a characteristic faint odour. It is soluble in benzene, chloroform, petroleum ether and acetic acid, while insoluble in cold and hot water and alcohol. It is insoluble in aqueous caustic soda and gives no coloration either on heating or prolonged standing. It is not volatile in steam and does not sublime. It dissolves in sulphuric acid (conc.) giving a deep red coloration, but on the addition of water the colour disappears and the original compound is reprecipitated. The compound gives deep yellow coloration with alcoholic caustic potash, thus definitely indicating the presence of a lactonic ring. From the alkaline solution acid precipitates the original compound. With alcoholic ferric chloride the compound gives a violet coloration showing the presence of a phenolic hydroxyl group. It fails to give Liebermann-Burchard reaction. The lactone neither gives any test with alkaline sodium nitroprusside nor reduces Tollen's reagent, a property mainly shown by  $\beta\gamma$ -unsaturated lactones. The compound is unsaturated and adds on bromine in benzene or acetic acid. The compound indicated the presence of no methoxyl group as found by Zeisel's method. [Found: C, 73.52; H, 7.21; M.W. (cryoscopic in phenol), 412, 415; M.W. (Rast's camphor method), 410.  $C_{26}H_{30}O_8$  requires C, 73.17; H, 7.31 per cent. M.W., 410].

Repeated attempts to prepare the silver, lead and copper salts of the compound were unsuccessful.

*Cedrelone Dibromide*.—The compound (1.5 g.) was dissolved in dry benzene (10 c.c.) and the mixture kept in a freezing mixture. To this was added an 1% solution of bromine in the same solvent in small amounts during the period of about half an hour till the bromine was in slight excess. During the addition the temperature was not allowed to rise above 0°. The mixture was kept overnight in the refrigerator, and the solvent and the excess of the bromine distilled off on the water-bath. The syrupy residue was dissolved in the minimum quantity of alcohol and a few drops of water added to the solution, when fine glistening orange needles settled down. The product was filtered,

washed with water and recrystallised from alcohol in beautiful yellow needles, m.p.  $116^{\circ}$ , yield 1.4 g. The compound is soluble in methyl and ethyl alcohols, ethyl acetate and benzene, but insoluble in hot or cold water. (Found: Br, 26.4, 28.09.  $C_{26}H_{30}O_5Br_2$  requires Br, 28.07 per cent).

*Acetylcedrelone*.—The compound (2 g.) was dissolved in acetic anhydride (10 c.c.), anhydrous sodium acetate (1 g.) added and the mixture gently refluxed in a boiling tube on a sand-bath for about 2 hours. After that the mixture was poured into cold water, well stirred and kept in the refrigerator for about 4 hours, when the acetyl derivative crystallised out in shining crystals. It was filtered and thoroughly washed with water and recrystallised from 80% alcohol in small colorless needles and plates, m.p.  $148^{\circ}$ , yield 2.01 g. The compound is soluble in alcohol, acetone, ethyl acetate, benzene, ether and petrol ether, but insoluble in water. (Found: acetyl, 11.4, 10.9.  $C_{25}H_{28}O_5.COCH_3$  requires acetyl, 9.51 per cent).

*Cedrelone Phenylurethane*.—Cedrelone (1 g.), dissolved in 5 c.c. of anhydrous benzene, was treated with phenyl isocyanate (2 g.), dissolved in 5 c.c. of the same solvent; the mixture was refluxed on the sand-bath for about 2 hours and then the solvent distilled off. The residue was allowed to cool when it became a syrup. This was dissolved in absolute alcohol and allowed to stand for some time when shining long needles melting at  $232^{\circ}$  were obtained. The compound is soluble in alcohol, benzene, ether and petrol-ether but insoluble in water. (Found: N, 2.32.  $C_{25}H_{29}O_4.OCONHC_6H_5$  requires N, 2.64 per cent).

*Cedrelone Monoxime*.—Hydroxylamine hydrochloride (1.5 g.) and anhydrous sodium acetate (3 g.) were thoroughly mixed together in a mortar and the mixture was taken in 25 c.c. of glacial acetic acid and heated for about half an hour on the sand-bath. To this was added cedrelone (8 g.) and the mixture was refluxed in a boiling tube for about an hour on a sand-bath. The mixture while hot was poured into cold water, when a crystalline mass settled down. It was filtered, thoroughly washed with water, dried and recrystallised from hot alcohol in shining colorless prisms and needles, m.p.  $258^{\circ}$ , yield 1.46 g. The compound is soluble in alcohol, acetone, ethyl acetate, but insoluble in water, ether and petrol-ether. (Found: N, 3.18.  $C_{25}H_{29}O_4.NOH$  requires N, 3.29 per cent).



## THORIUM : ITS SEPARATION FROM CERITE EARTHS AND ESTIMATION

BY M. VENKATARAMANIAH, T. K. SATYANARAYANAMURTHY AND  
BH. S. V. RAGHAVA RAO

Detailed procedures have been described for the separation of thorium from cerite earth mixtures in proportions approximately from 1:1 up to 1:10 using the reagents : trimethylgallic acid, phenoxy-acetic acid, veratric acid, benzoic acid, ammonium benzoate and tannic acid. Thorium in monazite has also been successfully estimated employing these reagents

The separation of thorium from the rare earths, particularly from the cerite earths, is one of the principle problems of thorium chemistry, since on the ease and effectiveness of this separation depends the commercial utilization of the element. Several methods have been suggested, but few have been investigated in any detail (Moeller *et al.*, *Chem. Rev.*, 1948, **42**, 63). In the following pages are presented results of systematic investigations on a number of reagents, many of which are now reported for the first time.

### EXPERIMENTAL

Each reagent was tried first on a solution of pure thorium, next on made-up mixtures of thorium and cerite earths, and finally on a sample of Travancore monazite.

The thorium solution was obtained by further purification of high grade thorium nitrate as follows. The thorium was twice precipitated with sebacic acid, and then with hydrogen peroxide. The oxide was dissolved in nitric acid, evaporated to dryness on a water-bath and finally dried to a constant weight in an air-oven at 100° to 120°. The thorium content of the sample was variously estimated with sebacic acid (Mitchel and Ward, "Modern Methods in Quantitative Chemical Analysis", 1932, p. 149), oxalic acid (Scott, "Standard Methods of Chemical Analysis", 1937, Vol. I, 5th Ed., p. 946) and potassium iodate in nitric acid (Meyer and Speter, *Chem. Ztg.*, 1910, **34**, 306). All procedures yielded results agreeing within 0.2%.

The cerite earth solution was prepared from monazite from which all thorium and the yttrium earths had been very carefully removed. The earth content was estimated by precipitation from an aliquot part with oxalic acid and weighing the ignited residue as oxides. No attempt was made to determine the proportion of the individual members in the group, neither would it serve any purpose in this investigation.

For the estimation of thorium in monazite, a sample from Travancore was digested according to the usual practice with sulphuric acid and taken up in ice-cold water. Oxalic acid in sufficient excess was next added and the oxalate precipitate was dissolved in fuming nitric acid and evaporated to dryness on a water-bath. The residue was taken up in water, made up to a definite volume, and aliquot portions were pipetted

out for each determination. It may be mentioned that attention was focussed not on an accurate analysis of monazite, but on the efficiency of the reagent as a means of separation of thorium from the rare earths.

*Trimethylgallic Acid.*—Neish (*Chem. News*, 1904, **90**, 196) made the observation that gallic acid in *alcoholic* solution precipitated thorium as a flocculent, slimy mass while holding other cerite earths in solution, but the subject was not further investigated. Some preliminary experiments conducted by us showed that while the precipitation of thorium was incomplete in both alcoholic and aqueous solutions, large amounts of the cerite earths were simultaneously carried down. On the other hand, trimethylgallic acid in neutral or faintly acid medium proved highly satisfactory. Neither ammonium gallate nor ammonium trimethylgallate, however, proved of any value.

The thorium solution was made just neutral to Congo red and diluted to 150 c.c. Solid ammonium chloride (20-25 g.) was then added and the solution heated to boiling. To this was added with constant stirring a slight excess of a boiling 2% solution of the reagent (i. e. about 100 c.c. of the precipitant for every 0.1 g. of the oxide). A gelatinous precipitate resulted which settled down rapidly. After about 15 minutes on a water-bath, the precipitate was filtered hot through Whatman No. 41, washed with a boiling 0.2% (approximately) solution of the reagent to which a few grams of ammonium chloride had also been added, *partially dried*, and ignited to the oxide. When the quantity of the cerite earths is rather large, the precipitate carries small quantities of these and a second precipitation, as described below, is necessary. The washed precipitate was returned to the original beaker, dissolved in the minimum of hot dilute hydrochloric acid, and dilute ammonia was very carefully added till the liquid reacted but faintly acid to Congo red. Precipitation, washing and ignition were repeated. Some representative results are shown in the following table.

TABLE I

ThO <sub>2</sub> taken.	Cerite earths R <sub>2</sub> O <sub>3</sub> added.	Wt. of ThO <sub>2</sub> obtained in single pptn.	Double pptn.
0.1180 g.	—	0.1181 g.	—
0.1180	—	0.1178	—
0.2360	—	0.2362	—
0.1180	0.1405 g.	0.1183	0.1181 g.
		0.1184	0.1182
0.1180	0.4580	0.1182 } slightly 0.1180 } coloured	0.1178 0.1182
0.1180	0.5620	0.1185 } slightly 0.1183 } coloured	0.1179 0.1180
0.1180	1.1450	0.1200 } 0.1208 } coloured	0.1180 0.1183
{ Monazite } 0.0900 }	0.4708	—	0.0900 0.0898

*Phenoxyacetic Acid*.—Pratt and James (*J. Amer. Chem. Soc.*, 1911, **33**, 1330) recorded that precipitation of thorium by phenoxyacetic acid in neutral solution was almost quantitative, while Smith and James (*ibid.*, 1912, **34**, 281) opined that the thorium salt was slightly soluble in water. A more detailed investigation appeared desirable. The following procedure yields good results.

The thorium solution, which should react neutral to Congo red, is diluted to 100 c.c. and heated to boiling. To the boiling solution is added slowly and with constant stirring a slight excess (100 c.c. for every 0.1 g. of  $\text{ThO}_2$  will be sufficient) of a hot 2% solution of phenoxyacetic acid. The liquid is now once again brought to boiling, and set aside to cool. The cooled precipitate is filtered through Whatman No. 41 and washed with a cold 0.2% (approx.) solution of phenoxyacetic acid. The washed precipitate is now returned to the original beaker and dissolved in the minimum of hot diluted (1:2) hydrochloric acid. The solution is diluted to about 100 c.c. and very carefully neutralised by dropping dilute ammonia until it is but faintly acid to Congo red. The thorium is reprecipitated, washed and ignited to the oxide. Some results are shown in the following table.

TABLE II

$\text{ThO}_2$ taken.	Cerite earths $\text{R}_2\text{O}_3$ added.	$\text{ThO}_2$ obtained.	$\text{ThO}_2$ taken	Cerite earths $\text{R}_2\text{O}_3$ added.	$\text{ThO}_2$ obtained.
0.1140 g.	—	0.1143 g.	0.1180 g.	0.5610 g.	0.1183 g.
0.1140	—	0.1140	0.1140	0.5712	0.1144
0.1180	—	0.1178	0.1140	0.5712	0.1146
0.1180	—	0.1181	0.1140	1.1424	0.1143
0.1180	0.1402 g.	0.1181	0.1140	1.1424	0.1145
0.1140	0.2805	0.1138			
0.1140	0.2805	0.1143	{ Monazite }		
0.1140	0.4580	0.1138		0.4708	0.0902 0.0901

*Veratric Acid*.—This reagent or any of its analogues has not been mentioned in literature. The thorium solution which should be nearly neutral to Congo red, is diluted to 100 c.c., solid ammonium chloride (15-20 g.) added and heated to boiling. To the boiling solution is added, with constant stirring, a saturated boiling solution of veratric acid. The resulting gelatinous precipitate is allowed to settle, filtered through Whatman No. 41 filter, washed with hot dilute veratric acid in 5% ammonium chloride, transferred to the original beaker, dissolved in dilute hydrochloric acid, diluted and reprecipitated. After complete washing the precipitate is ignited and weighed as oxide. Representative results are shown in Table III.

*Benzoic Acid*.—Benzoic acid was suggested by both Kolb and Ahrle (*Z. angew. Chem.*, 1905, **18**, 92) and Neish (*loc. cit.*). Apparently without further investigation the reagent was pronounced unsatisfactory and rejected in favour of *m*-nitrobenzoic acid, a rather expensive reagent. The following procedure adopted by us has yielded results which compare favourably with any known method.

TABLE III

ThO <sub>2</sub> taken.	Cerite earths R <sub>2</sub> O <sub>3</sub> added.	ThO <sub>2</sub> obtained.
0.1180 g.	—	0.1186 g. 0.1186
0.1180	1.1450 g.	0.1182 0.1179
{ Monazite } { 0.0900 }	0.4708	0.0904 0.0907

To the thorium solution, if strongly acid, dilute ammonia is added dropwise until the solution reacts but faintly acid to *methyl red*. It is then diluted to 200 c.c. and heated to boiling. Hot 1% benzoic acid solution (100 c.c.) is added with vigorous stirring followed by 5% ammonium acetate until the liquid reacts at this stage just neutral. A precipitate results which settles quickly. This is filtered through Whatman No. 41. After washing with hot 0.25% benzoic acid the precipitate is returned to the original beaker and dissolved in hot dilute nitric acid and precipitation is repeated. The second precipitate after complete washing is ignited and weighed as the dioxide. The results are shown in the following table.

TABLE IV

ThO <sub>2</sub> taken.	Cerite earths added.	ThO <sub>2</sub> obtained.
0.1140 g.	—	{ 0.1142 g. 0.1141
0.1140	0.4580 g.	{ 0.1141 0.1142
0.1140	0.5712	{ 0.1145 0.1148
0.1140	1.1424	{ 0.1148 0.1146
{ Monazite } { 0.0900 }	0.4708	{ 0.0900 0.0904

*Ammonium Benzoate*.—This reagent has not been referred to previously.

The nearly neutral solution is diluted to 200 c.c., acidified with 2 c.c. of glacial acetic acid and cold 3% ammonium benzoate is run in a thin stream with constant stirring until about 100 c.c. have been added for every 0.1 g. of thorium dioxide supposed to be present. The precipitate is now left on a water-bath and after it has settled (usually 30 minutes) as much of the supernatant liquid as possible is poured through a Whatman No. 41 filter, without disturbing the precipitate. It is now stirred up with hot 0.5% benzoic acid, filtered, and washed with the same reagent. The washed precipitate is transferred back to the original beaker and dissolved in a minimum of dilute hydrochloric acid. The solution is diluted to 150 c.c. and dilute ammonia is

run down from a burette until slight turbidity results. Precipitation is completed by adding a slight excess of ammonium benzoate reagent. The precipitate is next filtered, washed with hot 0.5% benzoic acid, and ignited to the oxide. The following table shows the results obtained.

TABLE V

ThO <sub>2</sub> taken.	Cerite earths R <sub>2</sub> O <sub>3</sub> added.	ThO <sub>2</sub> obtained.
0.1140 g	—	0.1142 g. 0.1141
0.1140	0.4580 g.	0.1141
0.1140	0.5712	0.1145 0.1148
0.1140	1.1424	0.1148 0.1146
{ Monazite 0.0900 }	0.4708	0.0900 0.0904
{ 0.0900 }	0.4708	0.0897 0.0900

*Tannic Acid.*— This reagent which has found such extensive use in the separation of columbium and tantalum does not seem to have attracted attention in this field. Neish (*loc. cit.*) refers to it only passinglly.

The neutral solution is diluted to 200 c.c. after addition of 10 g. to 15 g. of ammonium chloride. Dilute acetic acid is then added dropwise until a drop of the solution just turns Congo red paper blue. Mineral acids should not be used for this acidification. The solution is heated just to boiling (it should not actually boil), and hot 5% tannic acid solution at the rate of 100 c.c. per 0.1 g. of thorium oxide is added slowly with constant stirring. The precipitate is left on a water-bath for 2 hours after which it is filtered through Whatman No 41 and washed with 2% tannic acid solution to which a

TABLE VI

ThO <sub>2</sub> taken.	Cerite earths added.	ThO <sub>2</sub> obtd.	ThO <sub>2</sub> taken.	Cerite earths added.	ThO <sub>2</sub> obtd.
0.0570 g.	—	0.0572 g.	0.1140 g.	1.1424 g.	0.1143 g.
0.0570	0.4580 g.	0.0573	0.1140	1.1424	0.1140
0.0570	0.4580	0.0574	0.1180	—	0.1183
0.1140	—	0.1139	0.1180	0.1402	0.1183
0.1140	0.4580	0.1142			
0.1140	0.5712	0.1148	{ Monazite 0.0900 }	0.4708	0.0897 0.0900

little ammonium nitrate or chloride has been added. The precipitate with the filtered paper is transferred to the original beaker and boiled with about 40 c.c. of dilute HCl (1:2) to dissolve the precipitate. Nitric acid should not be used. After thorough digestion dilute ammonia is added until the liquid reacts just neutral to Congo red. Precipitation and washing are repeated and the washed precipitate is ignited to the oxide. The results are given in Table VI.

In all cases, however, zirconium and quadrivalent cerium, if present, are simultaneously precipitated, a disadvantage that is shared by many reagents for thorium. It is thus necessary that cerium is reduced to the trivalent stage and zirconium is removed earlier by a simple precipitation with oxalic acid.

ANDHRA UNIVERSITY  
WALTAIR.

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# DETERMINATION OF PEROXIDE VALUE OF RANCID FATS. A MODIFIED PROCEDURE

By S. MUKHERJEE

Peroxide value of the butter-fat has been determined by combining the method of Wheeler and Lea.

Peroxide value is by far the most extensively used index for evaluating rancidity of fats and oils. A number of different iodimetric procedures, viz., those of Lea (*Proc. Roy. Soc.*, 1931, 108B, 175), Wheeler (*Oil & Soap*, 1932, 9, 89) and Taffel and Revis (*J. Soc. Chem. Ind.*, 1931, 50, 87r) are available for making such determinations, and although all these methods are presumed to react quantitatively and may do under most conditions, results by the different methods are not always reliable. The experience of the present investigator with peroxide determination using the three methods is that Lea's method gives lower values than Wheeler's and still lower values are obtained with the Taffel-Revis's method. The results were found to differ depending on the following factors: (i) the atmosphere in which the estimation is carried out, (ii) the temperature, (iii) the time of reaction and (iv) weight of fat used in the estimation.

For this reason all the methods were subjected to re-examination using different weights of fat, different reaction period and using different temperatures, as also determinations were made both in presence of oxygen and in inert atmospheres. The experimental results with a sample of rancid butter-fat are tabulated below.

TABLE I

*Determination of peroxide value by different methods.*

1. Lea's method.				
Wt. of fat.	Time of reaction.	Temp.	Atmosphere.	Peroxide value.
1.008 g.	3 minutes	98.8°	Nitrogen	95.80
2.100	"	"	"	95.10
0.5020	"	"	"	95.88
0.2510	"	"	"	95.93
10.1000	"	"	"	93.05
2. Wheeler's method.				
5.5025 g.	1 minute	36-37°	Air	103.6
3.5163	"	"	"	104.7
7.8203	"	"	"	101.9
1.0035	"	"	"	104.5
10.0	"	"	"	98.0
3. Taffel-Revis method.				
1.0 g.	2-3 minutes	98.8°	CO <sub>2</sub>	91.81
2.0	"	"	"	89.62
5.0	"	"	"	88.01
10.0	"	"	"	86.82

From the results in Table I it is evident that the Wheeler method always gives higher values than the Lea or Taffel-Revis method. This can be explained firstly as due to the inert atmospheres maintained in the other two methods, whereas in the Wheeler method the atmospheric oxygen liberates a certain amount of iodine from the KI solution. The lower values in Lea's method may, however, be due to the fact that there is a possible chance of partial decomposition of the peroxides at the high temperature employed. The still lower values obtained with the Taffel-Revis method are probably due to the incomplete extraction of the peroxides with the acetic acid alone. The use of chloroform is a probable advantage with the Lea or Wheeler method. Thus a point of considerable importance in the peroxide determination is the *atmosphere* in which the reaction is conducted, as also the *temperature* of the reaction.

*The Effect of Weight of Fat.*—The next variable studied was the weight of fat used in the experiment, using a temperature of 36°-37° (Wheeler), an atmosphere of CO<sub>2</sub> (Taffel-Revis) and a reaction period of 2-3 minutes (Lea) and Table II shows the effect of sample size on the peroxide value.

TABLE II

*Peroxide value and sample size.*

Wt. of fat. (butter-fat).	Peroxide value.	Wt. of fat. (butter-fat):	Peroxide value.
0.1025	97.22	1.5129	96.83
0.2050	97.22	2.0100	96.02
0.4110	97.03	5.1035	93.0
1.0030	96.84	9.9877	92.85

TABLE III

*Effect of sample size on peroxide value.*

Coconut oil		Groundnut oil		Linseed oil	
Wt. of fat.	Peroxide value.	Wt. of fat.	Peroxide value.	Wt. of fat.	Peroxide value.
0.1230 g.	9.2	0.1532 g.	26.0	0.1028 g.	27.2
0.2526	9.2	0.3185	25.3	0.2550	25.9
1.0207	8.9	0.8241	23.5	0.7574	23.4
2.0512	8.8	1.5656	22.2	1.2022	20.2
5.0	8.1	2.9400	20.4	2.5110	18.2
		5.0	17.8	5.0	15.0

Comparison of the results obtained by Lea's method in Table I with those obtained in Table II clearly shows that in the original method of Lea there is a slight decomposition of the peroxide at the high temperature (about 1-2%). The peroxide value of a particular sample of oxidised fat is moreover found to vary considerably with the weight of the fat. This is probably due to the re-absorption of the liberated iodine at the unsaturated centres of the fat. This is more fully illustrated by the results in Table III where



similar experiments have been conducted with rancid coconut, groundnut, and linseed oils, the re-absorption of iodine by the oils being least with coconut and maximum with the linseed oil as the sample size is varied from 0.1 to 5.0 g. The error due to this source may be reduced by restricting the weight of the fat to the lower value employed in the Lea's method, viz. 1 g.

*Effect of Reaction Time.*—The next object was to study the effect of time factor on the peroxide value determinations. The following table (Table IV) records the results of such investigations using different reaction periods in the dark including those used by previous workers. In order to keep the weight of the fat constant and thus to minimise the effect due to this factor, nearly 1.0 g. of fat was used in these experiments, by taking the same measured volume of a chloroform solution containing a definite weight of the oxidised butter-fat.

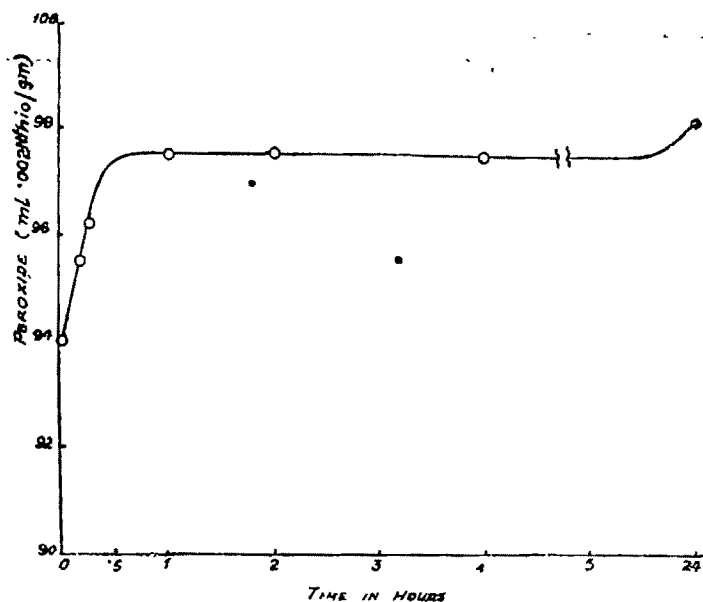
TABLE IV

*Peroxide values vs time.*

In CO<sub>2</sub> atmosphere at 37°.

Wt. of fat.	Time.	Peroxide value.	Wt. of fat.	Time.	Peroxide value.
1.0241	3.5 mins.	95.0	1.0460	2 hours	97.5
1.0460	10	95.5	"	4	97.5
"	15	96.2	"	6	97.5
"	30	97.3	"	12	97.7
"	45	97.5	"	24	98.2
"	60	97.5	"	48	98.93

Fig. 1



From the results in the above table it appears that almost 98% of the peroxide react within 3 to 5 minutes. For complete reaction of the peroxides with KI, it is better to allow one hour reaction time in the dark, as a safe measure. This is quite evident from the flat portion of the curve in Fig. 1 relating peroxide value and time factor.

*Recommended Procedure.*—For accurate determination of the peroxide the following procedure may therefore be used with advantage. About 1 g. of the oil or fat is weighed into a 750 c.c. glass-stoppered iodine bottle from which air has previously been excluded by flushing with carbon dioxide for 3 to 5 minutes, and 10 c.c. of a solvent comprising 40 parts of  $\text{CHCl}_3$  and 60 parts of acetic acid (glacial, A.R.) are added to dissolve the fat. The solvent mixture must previously be flushed with  $\text{CO}_2$  for 5 to 10 minutes before use to exclude any dissolved air; 2 c.c. of a saturated solution of KI is next added and the stopper, moistened with KI solution, is carefully put in place and the whole kept in the dark for one hour (at  $36^\circ\text{--}37^\circ$ ) after which the liberated iodine is titrated with  $N/200$ -thiosulphate solution after diluting the reaction mixture with oxygen-free distilled water. Lea's procedure for carrying out the titration in a dark room illuminated by a tungsten lamp is definitely an advantage in determining the end-point with the starch indicator. The result is expressed as ml. 0.002N- thiosulphate per g. of fat.

The method combines the essential features of the Wheeler's and Lea's method in that an inert atmosphere as used by Lea has been employed, the temperature used being that of Wheeler's, viz.  $36^\circ\text{--}37^\circ$ , at which the chance of decomposition of peroxide is nil and the weight of the fat has been confined to that used by Lea, viz. 1 g. to minimise the effect of re-absorption of iodine which will necessarily entail greater error when larger amount of fat is used, as in the original Wheeler's process. The results obtained by the modified method approach most closely to those obtained by Lea's method.

The author expresses his grateful thanks to Prof. M. N. Goswami for his deep interest in the work.

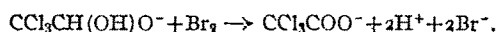
DEPARTMENT OF APPLIED CHEMISTRY,  
COLLEGE OF SCIENCE, CALCUTTA.

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## KINETICS OF THE REACTION BETWEEN CHLORAL HYDRATE AND BROMINE

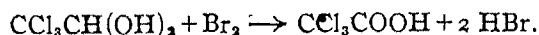
By A. N. KAPPANNA AND BHANU RAMCHANDRA DEORAS

The kinetics of the oxidation of chloral hydrate by bromine in aqueous solutions has been studied at 30° and 40°. The reaction has been found to take place according to the equation



The retarding influences of hydrogen and bromine ions on the velocity of reaction have been quantitatively studied. The energy of activation of the reaction has been found to be 15830 calories.

Bromine oxidises acetaldehyde to acetic acid in neutral solutions. In acid solutions, however, the reaction results in halogen substitution through a prototropic mechanism (Dawson, Burton and Aik, *J. Chem. Soc.*, 1914, 108, 1275). Trichloroacetaldehyde which exists in aqueous solution exclusively as chloral hydrate, does not offer any scope for substitution. The compound chloral hydrate is itself acidic in character and in acid solutions the only possible reaction with bromine is oxidation. Ogialoro (*Ber.*, 1874, 7, 1461) reported that chloral, when heated with bromine, formed the acid bromide,  $\text{CCl}_3\text{COBr}$ . Chlorine and bromine have been shown to react photochemically with chloral, yielding a number of oxidation products (Schumacher *et al.*, *Z. physikal. Chem.*, 1939, **B44**, 57; 1940, **B47**, 67). Kolthoff (*Pharm. Weekblad*, 1923, 60, 2) mentions that bromine does not oxidise chloral in acid solutions. It is well known that chloral hydrate molecule is stable only either in neutral or acid solutions and that alkaline solutions decompose rapidly (Enklaar, *Rec. trav. chim.*, 1905, 24, 419). Attempts to oxidise this compound keeping both the carbon atoms intact should therefore be made only in neutral or acid solutions. Preliminary experiments carried out in this laboratory showed that chloral hydrate reacted with bromine at measurable speeds at ordinary temperature and in equimolecular proportions. The quantity of acid formed, when decolorisation of a known quantity of bromine in presence of excess of chloral hydrate took place, was found on estimation to be equal to what should be expected if the reaction had taken place quantitatively according to the equation



The quantity of bromine taken up by a given quantity of chloral hydrate was likewise found to conform to the above equation. That trichloroacetic acid was formed was further proved by the decomposition of the resulting solution on boiling, yielding chloroform and carbon dioxide. We have studied the kinetics of the reaction and the results are reported in this paper.

### EXPERIMENTAL

Chemicals employed in this investigation were all of extra pure quality. The solutions were all prepared in redistilled water.

The reaction vessels were kept in an electrically regulated thermostat for all kinetic measurements. The reaction was followed by withdrawing definite volumes of reaction mixtures and estimating the unreacted bromine iodometrically.

Table I contains the results of an experiment carried out with a mixture containing 0.25 *M* chloral hydrate and 0.0054*N* bromine. The reaction mixture (10 c.c.) was titrated each time, after the addition of potassium iodide against *N*/200-thiosulphate.

TABLE I

Temp. = 30°.

Time.	Thio	$k_{\text{unl.}}$	Time.	Thio.	$k_{\text{unl.}}$
0 min.	11.90 c.c.				
		0.01440	72	5.50 c.c.	0.01969
15	9.30	0.01320	91	4.60	0.01042
30	8.00	0.01221	121	3.80	0.009407
50	6.45		160	3.00	0.00853

It will be seen that the unimolecular velocity constant falls off as the reaction progresses, more rapidly at the initial stages than at the later stages. This may be due, as is known in other cases of aqueous bromine oxidations, to the accumulation in the system of hydrogen and bromide ions and the retarding influence they exert. Tables II and III contain results of two experiments carried out to test the influence of each one of these two ions on the velocity of the reaction. Potassium bromide was added in one case and hydrochloric acid in the other, in such quantities that the concentrations of the bromine and the hydrogen ions in the respective mixtures could be regarded as constant through the course of the reaction. The concentrations of chloral hydrate and bromine were the same as in the previous experiment.

TABLE II

Temp. = 30°. KBr = 0.05*M*.

<i>t</i> .	Thio.	$k_{\text{unl.}}$
0 min.	10.90 c.c.	...
30	6.90	0.00907
46	7.40	0.008395
63	6.70	0.007705
87	6.70	0.007429
115	5.10	0.006578
188	3.60	0.005865

TABLE III

Temp. = 30°. Conc of HCl = 0.05*M*.

<i>t</i> .	Thio.	$k_{\text{unl.}}$
0 min.	13.50 c.c.	...
43	12.20	0.001736
85	11.45	0.001626
145	10.50	0.001548
234	9.20	0.001522
325	8.10	0.001488
455	6.85	0.001431

These results indicate that each of the ions, bromine and hydrogen, exerts powerful retarding influence, the effect of the hydrogen ion being more powerful. Each by itself is not sufficient to exert a steadying influence on the rate. The effect of the initial addition of sufficient excess of both potassium bromide and hydrochloric acid was next tried. The results are contained in Table IV.

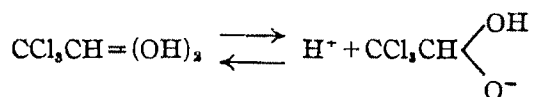
TABLE IV

Temp.=30° Chloral hydrate=0.20 M. Bromine=0.002854 N. HCl (initial)=0.008 N. KBr (initial)=0.0377 M. 25 c.c. titrated each time against N/400-thiosulphate.

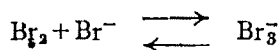
<i>t.</i>	Thio.	<i>k</i> <sub>uni.</sub>
0 min.	24.00 c.c.	
30	18.90	0.007951
45	16.70	0.008050
60	14.60	0.008027
75	13.15	0.008015
90	11.70	0.008000
121	9.20	0.007912

Mean 0.007993

The steady value of the velocity constant at the different stages of the reaction indicates clearly the role of the hydrogen and the bromine ions. The retarding influence of hydrogen ion is obviously due to the suppression of the ionisation of chloral hydrate and the consequent diminution of the effective concentration of the anion which appears to be the real reactant, in accordance with the equation,



Similarly, the bromine ion diminishes the effective concentration of free bromine by forming the tribromide ion according to the equation,



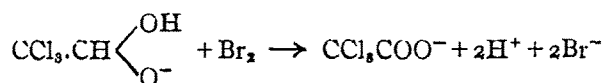
The order of the reaction with respect to chloral hydrate was determined by a set of experiments in which the initial concentration of this constituent was altered, while those of others were kept constant. Table V shows the variation of the velocity constant with increase in the concentration of chloral hydrate.

TABLE V

HCl=0.01N. KBr=0.02 M. Bromine=0.002 N.

Chloral hydrate (M)	...	0.05	0.10	0.15	0.20	0.25
<i>k</i> × 10 <sup>4</sup>	...	10.42	21.42	31.05	39.15	49.45

These results indicate, considering that it is the ion of chloral hydrate that is involved, the unimolecularity of the process with respect to chloral hydrate. The reaction can therefore be represented by the equation,



#### *Influence of Hydrogen-ion Concentration*

We chose sulphuric acid for the addition of hydrogen ion in all subsequent experiments as the addition of hydrochloric acid might introduce a complication by the formation of chloro-dibromide ion (Ray, this *Journal*, 1934, 11, 117).

Table VI contains results of a detailed study of the retarding influence of hydrogen ion.

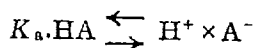
TABLE VI

Chloral hydrate = 0.25 M. KBr = 0.10 M. Bromine = 0.0025N.

Equiv. of H <sub>2</sub> SO <sub>4</sub> per litre	0.008	0.01	0.02	0.03	0.04	0.05	0.06
$k \times 10^4$	30.21	27.40	15.64	11.10	9.20	7.52	6.36

There is a progressive diminution in the velocity constant, as is to be expected if the anion is the reactant, with increase in the initial concentration of hydrochloric acid.

The concentration of the anion could be reckoned on the assumption that chloral hydrate behaves like a weak acid, HA, in the following way



where  $K_a$  represents the dissociation constant of the acid and HA, the concentration of the unionised acid. From which we can deduce

$$\text{A}^- = \frac{K_a \cdot (\text{HA})}{K_a + \text{H}^+}, \text{ where } (\text{HA}) \text{ is the total concentration of chloral hydrate.}$$

Introducing this in the kinetic expression,

$$\frac{dx}{dt} = k \cdot \text{CA}^- \times \text{CBr}_2 = \frac{k \cdot K_a \cdot (\text{HA})}{\text{H}^+ + K_a} \times \text{CBr}_2$$

=  $k_{\text{obs}} \times \text{CBr}_2$  for concentrations (HA) large in comparison with  $\text{CBr}_2$

$k_{\text{obs}}$ , the observed unimolecular velocity constant being equal to

$$\frac{k \cdot (\text{A}) \cdot K_a}{\text{H}^+ + K_a} = \frac{k' \cdot K_a}{\text{H}^+ + K_a} \quad \text{or} \quad \frac{1}{k_{\text{obs}}} = \frac{1}{k'} + \frac{\text{H}^+}{k' \times K_a}$$

This equation demands that we should get a straight line if we plot  $1/k_{obs}$  against  $H^+[H_2SO_4/2]$ . Actually we get a very good straight line with an intercept on the  $1/k_{obs}$  axis which should be equal to  $1/k'$ .  $1/k' = 1.20 \times 10^2$  and the slope of the line  $1/k'.K_a = 2.416 \times 10^4$  from which  $K_a$  comes out to be equal to  $4.96 \times 10^{-3}$ .

This value for the Ostwald constant for chloral hydrate would mean that chloral hydrate is a fairly strong acid. Chloral hydrate, even on very careful purification is definitely acidic in its reaction towards litmus and should be expected to be so by virtue of the two hydroxyl groups attached to the same carbon atom. But one could hardly believe that it could be as strong as monochloroacetic acid ( $K = 1.53 \times 10^{-3}$ ).

The molecular conductivity of chloral hydrate in 0.01 M solution is just 0.60 (Enklaar, *loc. cit.*) and it is a little difficult to reconcile this low conductivity with the high dissociation constant we arrive at on the basis of our kinetic study. We are investigating this matter further but we have to content ourselves at present by recording the observation we have made.

#### *Influence of Bromine Ion on the Reaction Rate*

The velocity of reaction, as observed before, is affected very considerably by the presence of bromide ion. This is obviously due to the removal of bromine from its free state by the formation of tribromide ion. The results of the experiments carried out at 30° and 40° with different concentrations of potassium bromide in the reaction mixtures are given in Table VII.

TABLE VII

Chloral hydrate = 0.20M.  $H_2SO_4$  = 0.01N. Bromine = 0.0025N.

KBr.	$k_{30} \times 10^3$ .	$k_{40} \times 10^3$ .	$k_{40}/k_{30}$ .	$\left[ k_{obs\ 30} \times \frac{k_{30} + Br}{k_{30}} \right]$ .	$\left[ k_{obs\ 40} \times \frac{k_{40} + Br}{k_{40}} \right]$ .
0.025 M	4.439	10.56	2.38	5.944	13.20
0.050	3.496	5.72	2.445	5.870	13.09
0.075	2.921	7.61	2.606	5.890	13.31
0.100	2.530	6.76	2.671	5.961	13.51
0.125	2.127	5.96	2.800	5.731	13.41
				Mean 5.879	13.304
				From graph $k' = 5.888$	13.510

The velocity constant falls off with increase in concentration of bromide ion. The equilibrium equation

$$K = \frac{(Br_2)_{free} \times Br^-}{Br_3^-} \quad \text{leads to the equation}$$

$$Br_2_{free} = \frac{K}{K + Br} \times Br_2_{total} \quad \text{expressing } Br_2_{total} = Br_2_{free} + Br_3^-.$$

The rate of reaction is proportional to the concentration of free bromine. Substituting this value for free bromine in the differential equation, we get

$$\begin{aligned}\frac{dx}{dt} &= k \cdot C_{A^-} \times C_{Br_2 \text{ free}} \\ &= k \cdot C_{A^-} \times \frac{K}{K + Br^-} \times C_{Br_2 \text{ total}} \\ &= k'' \cdot \frac{K}{K + Br^-} \times C_{Br_2 \text{ total}} \quad \text{where } k'' = K \cdot C_{A^-} \quad (C_{A^-} \text{ being in large excess}).\end{aligned}$$

$k_{\text{obs}} \cdot C_{Br_2 \text{ total}}$  ( $k_{\text{obs}}$  being the observed unimolecular constant) therefore

$$k_{\text{obs}} = k'' \cdot \frac{K}{K + Br^-} \quad \text{and}$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k''} + \frac{Br^-}{k'' \cdot K}$$

As should be expected from this equation we get very good straight lines on plotting  $1/k_{\text{obs}}$  against  $Br^-$  ( $KBr$ ) at both the temperatures.

We get this in spite of the fact that we have employed concentrations of potassium bromide instead of activities of bromide ion. The intercept  $1/k''$  at  $30^\circ$  has a value of  $1.70 \times 10^4$  or  $k'' = 5.888 \times 10^8$  and the slope  $1/k'' \cdot K_{30^\circ} = 23.0 \times 10^4$  from which we get  $K_{30^\circ} = 0.07386$ . Similarly  $1/k''$  at  $40^\circ$  gives  $0.74 \times 10^4$  or  $k'' = 13.510 \times 10^8$  and  $1/k'' \cdot K_{40^\circ} = 0.74 \times 10^5$  from which  $K_{40^\circ} = 0.100$ .

The values for  $K$  appear to be somewhat higher than what should be expected from the figures given by Linhart (*J. Amer. Chem. Soc.*, 1918, **40**, 158). The values for  $k'' = k_{\text{obs}} \cdot \frac{K + Br^-}{K}$  calculated from the observed velocity constants at different concentrations of potassium bromide are included in the 5th and 6th vertical columns of Table VII. The constancy at both temperatures is good and the average values agree very well with the intercepts from graphs.

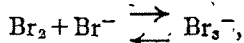
#### Temperature Coefficient of the Reaction Rate

Attention might here be drawn to the ratios  $k_{\text{(obs)}}_{40^\circ} / k_{\text{(obs)}}_{30^\circ}$  given in the 4th column of Table VII which show a steady rise with increase in the concentration of the retardant. This increase in temperature coefficient, signifying increase in energy of activation (which should be considered apparent energy of activation) is understandable as we know that the observed velocity constant involves the variable, concentration of bromide ion. The correct basis for the calculation of temperature coefficient is the value of  $k''$ .

$$\frac{k''_{40^\circ}}{k''_{30^\circ}} = \frac{13.510}{5.888} = 2.294.$$



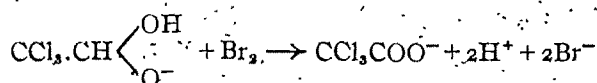
The energy of activation calculated from this value of temperature coefficient comes out to be 15830 cal. Similarly, the temperature coefficient of the equilibrium constant for the reaction



from the values of  $K$ , deduced from our measurements, leads to the value 5786 calories for the heat of reaction.

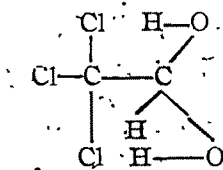
### DISCUSSION

The results recorded in the paper indicate the reaction to be comparatively simple and straight forward. The equation

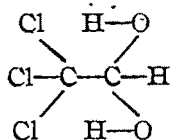


correctly represents the reaction kinetically and stoichiometrically. The process of oxidation consists in the removal of two hydrogen atoms from the chloral hydrate ion, as hydrobromic acid.

One of the hydrogen atoms is the hydroxyl hydrogen, ordinarily somewhat remotely situated from the other hydrogen which is directly linked to the carbon atom. The point of interest therefore is to account for the simultaneous removal of these hydrogens by an activated collision with a bromine molecule. Such removal could be facilitated only in case where the two hydrogens are situated in sufficient proximity to one another in such a manner that a bromine molecule colliding in suitable orientation could contact both. It is interesting to recall in this context, the structure proposed for chloral hydrate by Werner long ago (*J. Chem. Soc.*, 1904, 88, 1376) to account for the formation of chloroform and formic acid from this molecule



and compare it with the structure arrived at by Davies (*Trans. Faraday Soc.*, 1940, 86, 333) on the basis of infra-red studies.



The only apparent difference between the two, as depicted on paper, is in regard to the disposition of the hydrogen atom directly attached to the carbon atom. The infra-red evidence is that the hydroxyl hydrogens are clamped towards the chlorines joined to the  $\alpha$ -carbon atom. If we consider the actual locations of the three hydrogens in space with the hydroxyl hydrogens so clamped, it would be found that the

distance between the directly linked hydrogen and any one of the two hydroxyl hydrogens is small enough to enable a bromine molecule getting in between them to contact both. Hence, in the chloral hydrate ion, in which there is only one hydroxyl hydrogen, the simultaneous removal of this and the directly linked hydrogen by a single energised collision with a bromine molecule is possible, provided that the energy conditions are satisfied.

The energy of activation is of the magnitude usually met with in simple bimolecular reactions, indicating the effectiveness of a good number of collisions and consequently the facility with which the reaction seems to proceed.

PHYSICAL CHEMISTRY LABORATORY,  
COLLEGE OF SCIENCES, NAGPUR.

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## CYSTINE AND METHIONINE IN THE PROTEIN FROM THE SEEDS OF CARILLA FRUIT

By J. W. AIRAN AND N. D. GHATGE

Two sulphur-containing essential amino-acids, cystine and methionine, have been estimated in carilla fruit seed-cakes.

After the successive extraction of the seeds of Carilla fruit (*Momordica Charantia*, N.O. Cucurbitaceae) with organic solvents like petroleum ether, benzene, chloroform and alcohol, the residue was found to contain nitrogen and sulphur. The albumin, isolated from this residue according to the method adopted by Basu, Nath, Ghani and Mukherjee (*Ind. J. Med. Res.*, 1937, **24**, 4, 1027), was subjected to van Slyke's process (*J. Biol. Chem.*, 1911-12, **10**, 15) as modified by Plimmer and Rosedale (*Biochem. J.*, 1925, **19**, 1015) for the study of nitrogen distribution on the one hand, and Callan and Toennies method (*Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 450) for cystine estimation, and to Horn, Jones and Blum's method (*J. Biol. Chem.*, 1946, **166**, 313) for methionine estimation on the other. It contained 0.967% total sulphur, out of which 0.3647% was accounted for by cystine, and 0.3132% by methionine. The percentages of these essential amino-acids were 1.37 for cystine and 1.56 for methionine.

Since these seeds are not discarded in most of the preparations where the Carilla fruit is used as vegetable, these figures have a significance, and hence they are put along with the figures for some of the common seed meals below, the data being taken from Block and Bolling ("The Amino-acid Composition of Proteins and Foods", 1945, p. 195).

	%Cystine.	%Methionine.
Peanut meal	1.6	0.9
Cottonseed "	2.0	1.6
Soyabean "	1.3	1.3
Carilla seedcakes (present work)	0.0841	0.0957

### EXPERIMENTAL

**Total Sulphur.**—It was estimated by means of Parr's sulphur bomb; 0.2045 g. of protein yielded 0.01429 g. of barium sulphate which corresponded to 0.967% sulphur.

**Cystine.**—Protein (1 g.) and potassium permanganate (10 g.) were added to NaOH solution (6.4 g. in 150 c.c. water). The mixture was refluxed on a water-bath for 48 hours, after which period the excess of the permanganate was destroyed with methyl alcohol. It was then acidified and the insoluble portion filtered off. The filtrate was boiled with bromine water, and then the sulphate ions were precipitated as barium sulphate, and treated in the usual manner. The precipitate weighed 0.0266 g. which corresponded to 0.3647% sulphur in the sample, and hence to 1.37% cystine.

**Methionine.**—The protein (0.5594 g.) was refluxed on a sand-bath with 15 c.c. of 20% hydrochloric acid for 18 hours. After this period, the hydrolysate was concentrated to nearly 5 c.c. and then treated with a small quantity of vegetable charcoal, and filtered. The filtrate was then made to 100 c.c. and 50 c.c. of this solution were withdrawn and concentrated to 10 c.c. roughly. It was then filtered and made exactly to 10 c.c. and 2 c.c. of this taken for estimation. Three small glass bottles were taken; one of these was taken for the "blank" experiment, one for the "unknown", and the third for the "standard". For this estimation, an authentic sample of methionine was obtained from the B.D.H.

Into each of these the following reagents were added in the order given below :

"Blank".	"Unknown"	"Standard".
2 c.c. soln.	2 c.c. soln	2 c.c. soln.
3 c.c. distilled water	3 c.c. distilled water	3 c.c. dist. water
	1 c.c. sodium nitroprusside soln., 10%	1 c.c. sodium nitroprusside soln., 10%
1 c.c. 5N-NaOH soln.	0.1 c.c. 5N-NaOH soln.	0.1 c.c. 5N-NaOH

After these additions were made, the three bottles were shaken for 10 minutes and then to each of these, 2 c.c. of 3% glycine solution were added and again shaken for 10 minutes, and finally 2 c.c. of phosphoric acid were added. The bottles were then shaken and kept aside for 5 minutes.

The bottle marked "blank" did not develop any colour. The solutions from the other two bottles were then taken for comparison of their colours. The readings with the Dubosq colorimeter were :

1.	22 "unknown"	9.4 "standard"
2.	32.2 "	13.4 "
3.	35.6 "	15.2 "

2 C.c. of the "standard" taken for comparison contained 0.002 g. of methionine, whence the amount of methionine in the sample taken for analysis was 0.5594 g. or 1.529% in the protein. This would account for 0.3741% of the total sulphur.

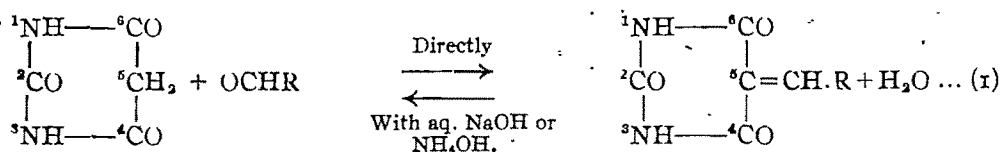
The albumin isolated was 6.135% of the seed-cake. Therefore the percentages of cystine and methionine in the seed-cakes work out to 0.0841 and 0.0957 respectively.

# A STUDY OF MALONYLGUANIDINE AND ITS REACTIVE METHYLENE GROUP. PART I. CONDENSATION OF MALONYLGUANIDINE WITH AROMATIC ALDEHYDES UNDER STRONG ACIDIC CONDITIONS

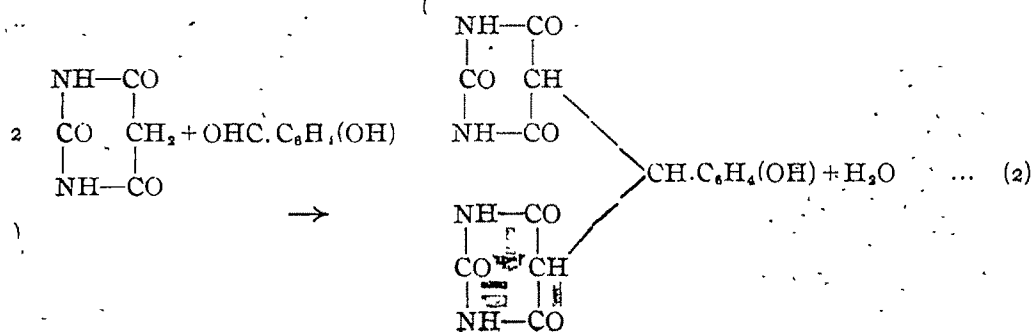
BY SUNIL KUMAR MUKHERJEE AND KUNJ BEHARI LAI, MATHUR

Malonylguanidine condenses with aryl aldehydes in the presence of acetic acid-sulphuric acid mixture (ca. 4:1) to give arylidene-malonylguanidine sulphates  $\text{ArCH} : [(\text{C}_4\text{H}_3\text{N}_3\text{O}_2) \cdot \text{H}_2\text{SO}_4]$ . In the presence of hydrogen chloride in saturation with absolute alcohol or acetic acid, the products are either an arylidene-malonylguanidine chloride  $\text{ArCH} : [(\text{C}_4\text{H}_3\text{N}_3\text{O}_2) \cdot \text{HCl}]$  or compounds of the *bis*-type  $\text{ArCH} : [(\text{C}_4\text{H}_3\text{N}_3\text{O}_2) \cdot \text{HCl}]_2$ , depending upon the nature of the aldehydes

Barbituric acid is known to give with aromatic aldehydes 5-arylidene-barbituric acids,



even by warming the ureide and the aldehyde in aqueous or alcoholic solutions and without the use of any condensing agent (Conrad and Reinback, *Ber.*, 1901, **34**, 1339; Weinschenk, *ibid.*, p. 1685). With thiobarbituric acid (Dox and Plaisance, *J. Amer. Chem. Soc.*, 1916, **38**, 2164) the 5-arylidene-2-thiobarbituric acids are smoothly obtained from aldehydes, but 12% hydrochloric acid is needed to effect condensation. Certain NN'-disubstituted barbituric acids and thiobarbituric acids (Whitley, *J. Chem. Soc.*, 1907, **91**, 1342; Akabori, *J. Chem. Soc., Japan*, 1931, **52**, 601; *Ber.*, 1933, **66B**, 139; Whitley and Mountain, *Proc. Chem. Soc.*, 1909, **28**, 121) can also be condensed more or less with the same ease as the parent ureides. It is remarkable that barbituric acid and salicylaldehyde upon direct condensation (Conrad and Reinback, *loc. cit.*, p. 1340) yield 5:5'-salicyl-bis-barbituric acid:



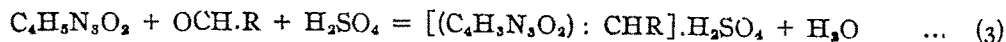
Condensation products from benzaldehyde and certain phenolic aldehydes in the presence of acetic acid are reported also to be of the *bis*-type (Pavoline, *Riv. Ital. essenze. Profumi*, 1933, 15, 171). In the above cases the condensation products are generally coloured, though in the case of less substituted aldehydes colorless forms are also met with. The compounds from the barbituric acids are decomposed with aqueous caustic soda or ammonium hydroxide with the separation of the aldehyde in a way, perhaps, typical of the reversal of an aldol reaction (cf. equation 1).

In comparison of barbituric acid, thiobarbituric acid and malonylguanidine as a quantitative precipitant for furfural in very dilute solutions, Dox and Plaisance (*J. Amer. Chem. Soc.*, 1916, 38, 2156) report incidentally the formation of furfurylidene-malonylguanidine  $C_4H_5OCH : C_4H_3N_3O_2$  in the presence of 12% hydrochloric acid. Apart from the above meagre reference little is known so far about the reactivity of malonylguanidine. In the present investigation the results obtained by condensing malonylguanidine with various aldehydes in alcohol and acetic acid under strong acidic conditions are recorded.

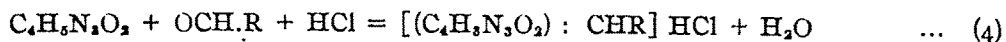
When malonylguanidine is reacted with benzaldehyde in the presence of glacial acetic acid-sulphuric acid mixture (4:1), a well defined crystalline product is obtained, which has the composition



the sulphuric acid remaining chemically bound to the condensation product. The acetic acid-sulphuric acid mixture serves also as a solvent for malonylguanidine which is difficult to dissolve in any other organic solvent except formic acid. Other aldehydes e. g., 4-chlorobenzaldehyde, anisaldehyde, salicylaldehyde, 3-hydroxybenzaldehyde, 4-nitrobenzaldehyde,  $\beta$ -resorcylic aldehyde, pyrogallol aldehyde and vanillin can be condensed with more or less equal ease giving products which are always coloured and contain combined acid. The latter is apparently released in cold water though by this treatment the solids invariably retain their original colour. On prolonged contact with water or upon heating, further decomposition occurs regenerating the malonylguanidine and the aldehyde. Decomposition is quicker with aqueous alkalis but is attended with the appearance of transient violet colorations in the case of phenolic compounds. All the products have the composition of an arylidene-malonylguanidine sulphate, formed thus,



Reaction can occur also when hydrogen chloride gas, dissolved in absolute alcohol or glacial acetic acid, is used as the condensing agent. But the nature of the product seems to depend upon the aldehyde used. Vanillin,  $\beta$ -resorcylic aldehyde, pyrogallol aldehyde and furfural give an arylidene-malonylguanidine chloride



in which curiously enough only one molecule of hydrochloric acid remains attached to the resulting product. On the other hand, benzaldehyde and 3-hydroxybenzaldehyde

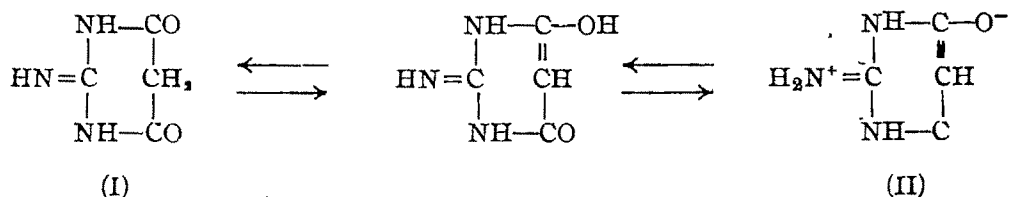
give compounds having the composition of a *bis*-malonylguanidine derivative



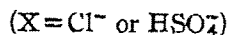
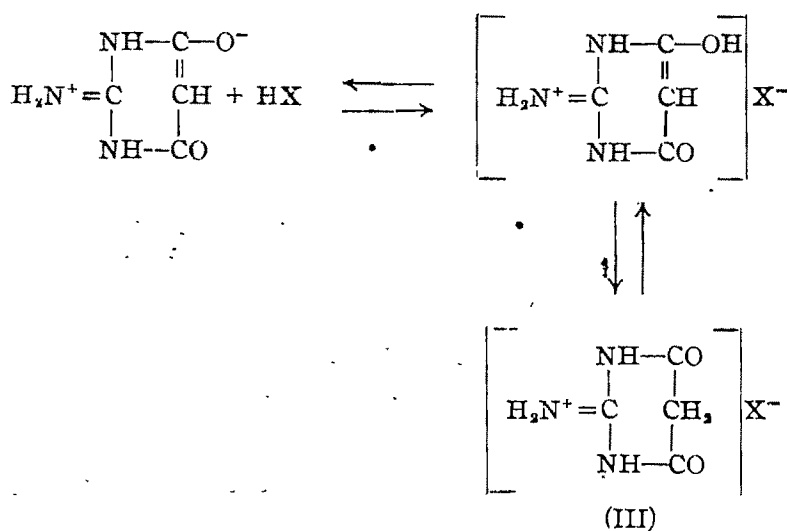
The arylidene-malonylguanidine chlorides behave more or less like their sulphate analogues but the *bis*-type of compounds are very soluble in cold water, though they also are hydrolytically decomposed with equal ease. The latter salts are, however, faintly coloured compared to the arylidene sulphates or chlorides, some of which are highly coloured.

The analogous mode of the hydrolytic decomposition of the products from malonylguanidine and from barbitruic acid is suggestive of the reactive methylene group in malonylguanidine being involved in the reaction. The unsaturated character of the arylidene-malonylguanidine sulphates and chlorides is in accord with this view point.

The above reactions can be explained if we consider that malonylguanidine is a "zwitterion" such as (II).



This internal salt-like arrangement is justified by the properties of malonylguanidine itself. As in the form (II) there is no incipiently ionised hydrogen atom, malonylguanidine is unable to condense with aldehydes directly like barbituric acid. However, in the presence of strong mineral acid, the zwitterion character is lost and a salt with the acid will be formed thus,



the glacial acetic acid or the alcohol serving the purpose of a solvent for the salt (III). In this way the reactive methylene group is made available for condensation, as it is in barbituric acid, with the difference that here a cation, e. g., from (III) is the reactive entity, instead of a neutral molecule. On this basis, the products holding only one equivalent of sulphuric acid (vide equation 3) should be deemed as acid salts. In an analogous way the *bis*-type of the compounds may also be formulated.

#### EXPERIMENTAL

*Preparation of Malonylguanidine.*—It was best prepared and purified according to the method of Dass and Dutt (*Proc. Nat. Acad. Sci. India*, 1939, 9, 93) from malonic ester and guanidine carbonate. In addition malonylguanidine was found to dissolve in warm (80°) formic acid from which it could be recrystallised; it failed to dissolve in several other non-polar solvents tried.

Malonylguanidine did not condense with benzaldehyde in the presence of absolute alcohol. The addition of sodium ethoxide evolved ammonia on continued heating indicating the occurrence of secondary decompositions. The use of glacial acetic acid or acetic anhydride was equally ineffective. Also, in the bare solvents used the malonylguanidine had remained practically insoluble. Finally, the following acidic mixtures were found to give products of uniform composition and had the added advantage of serving as a solvent for malonylguanidine:

- (i) Conc. sulphuric acid (25 c.c.) diluted to 100 c.c. with glacial acetic acid.
- (ii) Absolute alcohol saturated with hydrogen chloride gas.
- (iii) Glacial acetic acid saturated with hydrogen chloride gas.

*Condensation of Malonylguanidine with Benzaldehyde in the presence of Glacial Acetic Acid-Sulphuric Acid Mixture.*—The acid mixture (12.7 c.c.) was added quickly to malonylguanidine (1.27 g., 0.01 M) with vigorous stirring and slight warming on the water-bath, when all the guanidine practically went in solution. If the required amount of the solvent was not used at once, a part of the malonylguanidine tended to form a gelatinous product which failed to be redissolved in excess of the solvent. The clear liquid was decanted off from a few undissolved particles into a boiling tube containing a solution of benzaldehyde (1.6 g., 0.015 M) in glacial acetic acid (5 c.c.) and the mixture was heated on a water-bath at 80°-90° with occasional stirring. After 10 minutes, yellow feathery crystals began to appear, which increased considerably afterwards. Upon cooling, the whole crop of crystals was filtered, washed repeatedly with glacial acetic acid till the washings ceased to give any precipitate with aq. barium chloride. They were then further washed with carbon tetrachloride to remove acetic acid and dried at 90°. The product was pure enough but could be recrystallised from formic acid.

The compound was light yellow, showing leaflets under the microscope, m.p. 236-38° (decomp.). It decolorised quickly 1% potassium permanganate and bromine water in the cold. On boiling with water it decomposed to give a strong smell of



benzaldehyde and the aqueous filtrate gave a precipitate with barium chloride. The latter test could also be obtained from a suspension of the compound in cold water. Dissolution occurred also in aqueous alkali and concentrated sulphuric acid; it was followed by decomposition in the first case and colour change to golden yellow in the last case. {Found: N, 12.3;  $\text{H}_2\text{SO}_4$  (after aq. decomp.), 30.21.  $[\text{C}_6\text{H}_5\text{CH} : \text{C}_4\text{H}_3\text{N}_3\text{O}_2] \cdot \text{H}_2\text{SO}_4$  requires N, 13.41;  $\text{H}_2\text{SO}_4$ , 31.4 per cent). Yield 1.68 g. (56%).

*Preparation of various Arylidene-malonylguanidine Sulphates.*—Condensations were run, as in the previous experiment, with various aldehydes (0.015 to 0.02M). Of all the solvents tried formic acid had excellent solvent properties for the resulting products, which themselves had crystallised out from the reaction mixture more or less in the pure form. They were decomposed by hot water and aqueous alkalis, with the evolution of strong characteristic smell of the aldehyde, e. g., in the compounds with 4-chloro-, 4-methoxy-, 2-hydroxy-, 3-methoxy-, and 4-hydroxybenzaldehydes. Concentrated sulphuric acid dissolved them giving yellow-orange solutions. With phenolic compounds, however, aqueous alkali gave also transient violet colorations and concentrated sulphuric acid produced charring. The compounds from 3-hydroxy-, 4-methoxy-, 3-hydroxy-4-methoxybenzaldehydes were also slightly soluble in ether, chloroform and hot acetic acid. In every case the products decolorised 1% potassium permanganate. The test for unsaturation with bromine water, as applied to the non-phenolic compounds, was also given. Table I summarises the chief results obtained, those from benzaldehyde being also incorporated for the sake of completeness.

*Condensation of Malonylguanidine with Benzaldehyde and 3-Hydroxybenzaldehyde in the presence of Absolute Alcohol saturated with Hydrogen Chloride.*—The malonylguanidine (0.635 g., 0.005 M) was gradually dissolved in alcoholic hydrogen chloride (35 c.c.) and after filtration from a few undissolved particles, reacted with a solution of benzaldehyde (0.53 g., 0.005 M) in acetic acid (3 c.c.) in a boiling tube. The mixture was stirred and warmed at 40°-50° and kept overnight. The crystals that had separated were washed first with acetic acid and then repeatedly with chloroform till the washings ceased to give a precipitate with aqueous silver nitrate. They were then dried at 90°.

The compound had a faint yellow colour. It charred at 244° and decomposed with frothing at 256°. It was very soluble in cold water which deposited white granular mass on keeping. By this treatment also the aqueous liquid smelt freely of benzaldehyde. The aqueous filtrate gave a precipitate with aqueous silver nitrate, insoluble in nitric acid. Decomposition was quicker with aqueous alkalis. It dissolved in formic acid and concentrated sulphuric acid with evolution of hydrogen chloride in the latter case. {Found: N, 19.82; HCl (after alkaline decomposition and weighed as AgCl), 17.7.  $\text{C}_6\text{H}_5\text{CH} : [\text{C}_4\text{H}_4\text{N}_3\text{O}_2 \cdot \text{HCl}]_2$  requires N, 20.24; HCl, 17.58 per cent}. Yield 0.7 g. (61.3%).

In a similar experiment with 3-hydroxybenzaldehyde (0.91 g., 0.075 M) crystals appeared after 1½ hours at room temperature and the reaction was completed by keeping overnight. The product has its properties like the compound with benzaldehyde, m.p. 242-46° (decomp.). {Found: N, 19.5; HCl, 17.1.  $\text{HO} \cdot \text{C}_6\text{H}_4\text{CH} : [(\text{C}_4\text{H}_4\text{N}_3\text{O}_2 \cdot \text{HCl})_2]$  requires N, 19.03; HCl, 16.93 per cent}. Yield 0.9 g. (67.1%).

TABLE I

Ar-CHO & wt.	Formation of the compound.	Yield.		Colour, shape & decomp. point.	Arylidene-malonylguanidine sulphate. (Ar*CH : C <sub>4</sub> H <sub>3</sub> N <sub>3</sub> O <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> )			
					Nitrogen		H <sub>2</sub> SO <sub>4</sub>	
					Found.	Calc.	Found.	Calc.
C <sub>6</sub> H <sub>5</sub> .CHO (Benzaldehyde 1.6 g., 0.015 M)	After 10 mins. heating	1.68 g.	56.0%	Yellow leaflets; decomp. 236-38°	12.30	13.41	30.21	31.40
(Cl).C <sub>6</sub> H <sub>4</sub> .CHO 4 1 (1.4 g., 0.01 M)	After 5 mins. heating.	2.20	63.1	Yellow star-like crystals; decomp. 251-52°	12.44	12.05	—	—
(CH <sub>3</sub> O).C <sub>6</sub> H <sub>4</sub> .CHO 4 1 (Anisaldehyde, 2.04 g., 0.015 M)	After 10 mins. heating.	23.1	67.6	Golden yellow leaflets; charred 240°; decomp. 247°	12.02	12.24	28.71	28.57
(OH).C <sub>6</sub> H <sub>4</sub> .CHO (Salicylaldehyde, 2.84 g., 0.02 M)	Heated for 1 hr. & kept overnight.	1.90	55.1	Yellow feathery leaflets; charred 220°; decomp. 266°	12.71	12.76	30.34	29.80
(OH).C <sub>6</sub> H <sub>4</sub> .CHO 3 1 (1.84 g., 0.015 M)	After 20 mins. heating.	2.38	71.6	Yellowish green leaflets; charred 134°; decomp. 300°	12.84	12.76	28.81	29.80
(NO <sub>2</sub> ).C <sub>6</sub> H <sub>4</sub> .CHO 4 1 (2.27 g., 0.015 M)	Heated for 3 hrs. & kept for 3 hrs.	0.62	17.2	Pale yellow leaflets; decomp. 218°	16.70	15.64	27.09	27.30
(OH) <sub>2</sub> .C <sub>6</sub> H <sub>3</sub> .CHO 2:4 1 (β-Resorcylic aldehyde**, 1.38 g., 0.01 M)	Heated for 2 hrs; pptd by Ac <sub>2</sub> O (1 c.c.) & AcOH (10 c.c.) & warmed.	1.50	34.9	Dark red; charred 270°; soln. in hot ACOH, green fluorescence	8.63	9.79	23.45	22.84
(HO) <sub>3</sub> .C <sub>6</sub> H <sub>2</sub> .CHO 3:4:5 1 (Pyrogallol aldehyde)	After 40 mins. heating.	1.80	50.0	Tiny red plates; charred 220°	11.11	11.60	27.32	27.14
(CH <sub>3</sub> O)(OH).C <sub>6</sub> H <sub>3</sub> .CHO 3:4 1 (Vanillin, 2.28 g., 0.015 M)	After 10 mins. heating.	1.70	48.0	Yellow leaflets; charred 260°; decomp. 270°	11.54	11.69	27.80	27.30

*Condensations of Malonylguanidine with 2:4-Dihydroxy-, 3:4:5-Trihydroxy-, 3-Methoxy-4-hydroxybenzaldehydes and with Furfural.*—The condensations were run exactly as in the previous experiment, with malonylguanidine (0.635 g., 0.005 M). In the case of vanillin glacial acetic acid, saturated with hydrogen chloride, gave equally good result. All the products were decomposed by water giving the combined acid and the aldehyde back. Concentrated sulphuric acid and formic acid dissolved them with the evolution of hydrogen chloride in the former case and colour change to golden yellow in the latter case. Aqueous alkalis produced transient red-orange colorations in the case of the di- and tri-phenolic compounds. All the products had deeper colour than the bis-type of compounds and their composition tallied rather with an arylidene-malonylguanidine chloride. The results are summarised in the following table.

\* This 'Ar' is the same as signified by that of the aldehyde used.

\*\* The figures agreed with that of a diacetylated reaction product.

TABLE II

Ar-CHO & wt.	Formation of the compound.	Yield		Colour, shape & charring point.	Arylidene-malonylguanidine chloride. (Ar*CH: C <sub>4</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub> .HCl) Nitrogen HCl			
					Found.	Calc.	Found.	Calc.
(HO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> .CHO <sub>2:4</sub> <sub>1</sub> (β-Resorcylic aldehyde** 1.035 g., 0.075 M)	After 1½ hrs. at room temp.	1.10 g.	77.40%	Deep yellow; charred 241-42°	15.01	14.81	12.30	12.87
(HO) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> .CHO <sub>3:4:5</sub> <sub>1</sub> (Pyrogallol aldehyde, 1.16 g., 0.075 M)	After 1½ hr. at 40°	1.10	73.3	Orange blocks; charred 202°	13.87	14.02	11.92	12.20
(CH <sub>3</sub> O)(OH)C <sub>6</sub> H <sub>3</sub> .CHO <sub>3</sub> <sub>4</sub> <sub>1</sub> (Vanillin, 0.76 g., 0.005 M)	Within ½ hr. at 60°	0.58	32.2	Tiny red plates, charred 221°	14.13	14.11	11.15	12.00
C <sub>4</sub> H <sub>3</sub> O.CHO (Furfural, 0.72 g., 0.075 M)	Within 20 mins.	0.66	53.7	Carbonised, greenish black, infusible.	15.4	17.39	11.32	15.10

\* This 'Ar' is the same as signified by that of the aldehyde used.

\*\* Solution in formic acid of the product diluted with acetic acid gave bluish fluorescence.

Reactions in aqueous solutions under strong acidic conditions are proposed to be further investigated.

The authors' grateful thanks are due to Dr. S. Dutt for suggesting this piece of work and for his continued interest in it.

CHEMICAL LABORATORIES,  
UNIVERSITY OF DELHI,  
DELHI.

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## REVIEWS

**Die Thermodynamik des Wärme – Und Stoffaustausches in der Verfahrenstechnik—**  
Von Dr.-Ing. Werner Matz—Verlag Dr. Dietrich Steinkopff—Frankfurt (Main)—1949 ;  
pp. 355 + xii, Figs. 114. Price 30 D.M. (approximately).

This is a book on Thermodynamics of Exchange of Heat and Matter that take place in industrial processes, e. g., evaporation, distillation, absorption, adsorption, extraction, heating, cooling, etc. Exchange of heat and exchange of material between different parts of a system have been treated together. Scattered throughout the literature are to be found thermodynamic treatment of the processes mentioned before ; but here, in one single volume, all these processes have been dealt with from the same point of view. The author has restricted himself only to the processes peculiar to chemical industries and has not touched on operations like expansion, compression, refrigeration, flow of fluids, etc., which form the subjects of most books on chemical engineering thermodynamics. Treatment of the subjects selected is thorough and rigorous. The author has laid special emphasis on the Law of Conservation of matter, the first two Laws of Thermodynamics, and Dimensional analysis. The Second Law has been applied with the help of extrophy-concept.

All lovers of thermodynamics will find the book interesting and instructive. It may specially be recommended to chemical engineers and industrial chemists who want to acquire more intimate knowledge of the processes they handle. Considering the excellence of the book it is expected that in near future an English translation will come out from America.

H.L.R.

**High Polymer Physics: A Symposium—**Edited by Dr. Howard A. Robinson.  
Pp. 572 + xiii. Published under the auspices of the American Institute of Physics by the Chemical Publishing Co. Price \$12.00.

High Polymer study has during recent years come into great lime light. The developments have been so rapid that it is very difficult for any investigator to keep abreast of the huge mass of informations on its various aspects that are accumulating in the scattered literature on the subject. Unlike the chemical substances having small molecules, macromolecular substances are of importance mainly for their physical characteristics. It has therefore been very opportune for the High Polymer Branch of the American Physical Society, of which Dr. Howard A. Robinson was the Chairman, to arrange a symposium on High Polymer Physics and to publish the papers contributed there on. The contributions are from most of the leading investigators in the various branches of high polymer in America and cover a wide range of aspects of the subject. Many of the articles were scattered over a large number of Journals, but they have been revised by the authors to take into account the developments in the intervening periods. This, therefore, serves as a quite handy collection of very useful informations to one desiring to pursue the subject. The twentythree papers that have been contributed are divided into four parts. The first part deals with Determination of the Molecular Structure of High Polymers and includes the uses of colour and

Fluorescence indicators, applications of Infra-red methods and X-ray diffraction methods for determinations of structures. The articles on the physical properties of high polymers form the second and the largest part and deals with such topics as Mechanical properties, Equation of state, Viscometric investigations, Formation of ionised water films, Thermal behaviour, creep, permanent set and electrostatic properties. The third part deals with the Chemical Physics of the high polymers. The fourth part contains articles on the apparatus for the measurements of thermal diffusion and light scattering.

The articles are contributed by the leading investigators on high polymers in their own lines of research and as such they are in general very well presented and give a clear and up-to-date account of the aspects dealt with. Being reports of a symposium it cannot, however, be expected to give a connected account of the whole subject. Some of the articles presupposes a considerable amount of preliminary knowledge of the subject; Eyring's paper on "The mechanical properties of textiles" may be particularly mentioned in this connection. On the whole, the book will prove to be an asset to workers on high polymers and Dr. Robinson may be congratulated for his bringing out such a useful volume.

K. B.

**Gmelins Handbuch der Anorganischen Chemie.**—8 Auflage (Edition). System Number 18, Antimon. Teil B 2. Pp. 496.

In this volume the treatment of the physical properties of antimony, not dealt with in the previous volume, has been concluded.

This comprises a part of the electrical properties of the metal; addition and correction to the physical properties described in the previous volume; chemical properties of the element; its detection and estimation; the various compounds of antimony with hydrogen, oxygen, nitrogen, fluorine, chlorine, bromine and iodine.

All references to literature till the middle of 1948 have been fully considered.

Gmelins Handbuch of Inorganic Chemistry enjoys the same reputation and position as those of Beilstein's Handbuch for Organic Chemistry. The present volume also thoroughly maintains this tradition.

No university or research institute of chemistry can afford to miss this volume in their library.

P. R.

**Modern Plastics**—by Harry Barron. Published by Chapman & Hall. 2nd Edition, revised & enlarged. Pp. 778; price 50 Shillings.

This century has provided the background for an enormous expansion of the plastics industry. Technical and scientific knowledge regarding plastics is, however, still confined to a few scientists and competent technicians.

The spread of technical education is imperative for the healthy growth of any major industry. This book has been written with a view to removing the lack of knowledge on Plastics as the author rightly thinks that "Lack of knowledge and lack of efforts results in the facile and disastrous industrial policy of purchasing foreign licenses for processes and goods. This is the easy way out but it subsidises foreign developments and effectively stifles one's own".

The book, divided into 5 parts (each subdivided into several chapters) dealing respectively with (I) Raw materials for plastics and Theory of plastics formation, (II) Thermosetting resins and their plastics, (III) Cellulose Plastics, (IV) Vinyl Plastics, (V) Glyptal, Casein, Silicone and Polyamide plastics, (VI) Analytical aspects and Physical Testing of plastics, provides a considerable amount of technical information which though seemingly "somewhat sketchy to the erudite" is adequately comprehensive and of much practical value.

The presentation of the subject is well balanced.

B. K. M.

**Chyma : Annual Studies in the History of Chemistry, volume II.** Editor in Chief: Tenney L. Davis. Published by the University of Pennsylvania Press, Philadelphia, 1949.

Chymia is rendering a great service to the History of chemical science of the world in publishing authoritative articles of well reputed authors on the subject ; some of them are professors of the History of Science and curator of research institutes. It appears like the first volume of this study to be less representative so far as chemistry in ancient India is concerned. Even in the article on "The experimental origin of chemical, atomic and molecular theory before Boyle," Professor Hooykoas has not unfortunately mentioned anything about the theory of atom in Indian philosophical science, though it is very likely that the Greeks imbibed the idea of atoms from the Indians.

R. C.

**Quarterly Reviews**—Vol. II, No. 1, 1948. Pp. 91. Price 8/- Sh. The Chemical Society, London.

These reviews are being published by the Chemical Society. The present issue which forms No. 1 of Vol. II deals with the recent development of our knowledge on the following subjects :—

1. Disproportionation in Organic Compounds.
2. The Chemistry of Silicon Polymers.
3. Physiologically active unsaturated Lactones.
4. Far Ultra-violet Spectra, Ionisation Potentials and their Significance in Chemistry.

As these reviews have been made by competent workers in the respective field, they will undoubtedly be found very useful by all advanced students and workers in chemistry. And as such they should find a place in all scientific libraries.

P. R.

IMIDOCHLORIDES. PART IX. REACTION OF AROMATIC ANILIDE  
IMIDOCHLORIDES WITH ETHYL SODIOACETOACETATE: SYNTHESIS  
OF SOME 4-HYDROXY-2-ARYL-3-ACETYLQUINOLINES

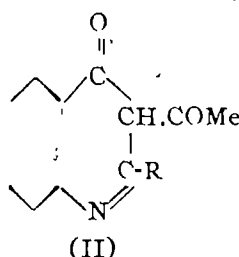
By S. A. KULKARNI AND R. C. SHAH

Desai and Shah (this *Journal*, 1949, 26, 121) achieved the synthesis of otherwise inaccessible 4-hydroxy-2-phenyl-3-acetylquinolines by the condensation of benzanilide imidochlorides with ethyl sodioacetoacetate. In extension of this work imidochlorides derived from simple anilides of *o*-, *m*-, and *p*-toluic acids, *m*-, *p*-bromobenzoic acids, *p*-chlorobenzoic acid,  $\alpha$ - and  $\beta$ -naphthoic acids have been condensed with ethyl sodioacetoacetate, and the crude condensation products obtained were cyclised to the corresponding 4-hydroxy-2-aryl-3-acetylquinolines.

Desai and Shah's condensation of benzanilide imidochloride with ethyl sodioacetoacetate has led to the synthesis of the hitherto unknown 4-hydroxy-2-phenyl-3-acetylquinoline (Desai and Shah, this *Journal*, 1949, 26, 121). The synthesis appears to be general as imidochlorides derived from the benzoyl derivatives of mono-substituted anilines and also of  $\alpha$ - and  $\beta$ -naphthylamines condense with ethyl sodioacetoacetate affording ultimately the corresponding 4-hydroxy-2-aryl-3-acetylquinolines (Desai and Shah, *loc. cit.*).

In extension of the above work, imidochlorides derived from the simple anilides of *o*-, *m*-, and *p*-toluic acids, *m*- and *p*-bromobenzoic acids, *p*-chlorobenzoic acid, *m*- and *p*-nitrobenzoic acids and  $\alpha$ - and  $\beta$ -naphthoic acids have been condensed with ethyl sodioacetoacetate. The condensation was carried out under the conditions of Desai and Shah (*loc. cit.*). The condensation products could not be crystallised and were directly cyclised by heating under reduced pressure, when the corresponding 4-hydroxy-2-aryl-3-acetylquinolines (I, R=aryl), viz., 4-hydroxy-2-, *o*-, *m*-, *p*-tolyl-3-acetyl-; 4-hydroxy-2-*m*- and *p*-bromophenyl-3-acetyl-; 4-hydroxy-2-*p*-chlorophenyl-3-acetyl-; and 4-hydroxy-2- $\alpha$ - and  $\beta$ -naphthyl-3-acetylquinolines respectively were obtained, all of which are new. The crude condensation products obtained from *m*- and *p*-nitrobenzanilide imidochlorides could be cyclised neither by heating under reduced pressure nor by heating them in diphenyl ether solution (*vide infra*).

The present investigation shows that the presence of a substituent in the acid part of the molecule does not appreciably affect either its condensation with ethyl sodioacetoacetate or the cyclisation of the crude condensation product to the quinoline derivative, thereby showing the general applicability of the synthesis.

CC(=O)C1=C(O)C=CC=C1N=C1C=CC=CC=C1  
(I)

## EXPERIMENTAL

2,4-Dinitrophenylhydrazone was obtained as orange needles, m.p. 292°. (Found : N, 16.0.  $C_{24}H_{10}O_5 N_5$  requires N, 15.4 per cent).



4-Hydroxy-2-*m*-tolyl-3-acetylquinoline was prepared from *m*-toluanilide imidochloride in 10% yield (b. p. 185°-195°/8 mm. and 183°-188°/4 mm., Kulkarni and Shah, *loc. cit.*), as colorless needles m.p. 279-80°. (Found : N, 5.4.  $C_{18}H_{15}O_2$  N requires N, 5.0 per cent).

2:4-Dinitrophenylhydrazones were obtained as orange coloured needles, m. p. 297°. (Found : N, 15.6.  $C_{24}H_{10}O_5$  N<sub>2</sub> requires N, 15.4 per cent).

4-Hydroxy-2-*p*-tolyl-3-acetylquinoline was prepared in 12% yield from *p*-toluanilide imidochloride (b. p. 207°/24 mm., Kulkarni and Shah, *loc. cit.*) as colorless needles, m.p. above 297°. (Found : N, 5.1.  $C_{18}H_{15}O_2$  N requires N, 5.0 per cent).

2:4-Dinitrophenylhydrazones, m.p. above 300°. (Found : N, 15.2.  $C_{24}H_{10}O_5$  N<sub>2</sub> requires N, 15.4 per cent).

4-Hydroxy-2-*m*-bromophenyl-3-acetylquinoline was prepared in 13% yield from *m*-bromobenzanilide imidochloride (b. p. 250°-260°/60 mm., Kulkarni and Shah, *loc. cit.*), m. p. 257-59°. (Found : N, 4.2.  $C_{17}H_{12}O_2$  NBr requires N, 4.1 per cent).

2:4-Dinitrophenylhydrazones were obtained as orange needles, m. p. 296-97° (decomp.). (Found : N, 13.6.  $C_{23}H_{10}O_5$  N<sub>2</sub> Br requires N, 13.5 per cent).

4-Hydroxy-2-*p*-bromophenyl-3-acetylquinoline was prepared in 5% yield from *p*-bromobenzanilide imidochloride (Shah and Chaubal, *J. Chem. Soc.*, 1932, 652) and crystallised from ethyl alcohol, m. p. 280-82°. (Found : N, 4.2.  $C_{17}H_{12}O_2$  NBr requires N, 4.1 per cent).

*p*-Chlorobenzanilide Imidochloride.—Dry *p*-chlorobenzanilide (10 g.) and phosphorus pentachloride (10 g.) were intimately mixed and heated on a water-bath till the evolution of hydrochloric acid ceased. The hot clear liquid was poured in about 30 c.c. of sodium-dried petroleum ether (b.p. 60°-80°), cooled externally by ice. The precipitated *p*-chlorobenzanilide imidochloride was quickly filtered through dry funnel, washed thoroughly with petroleum ether and dried in vacuum, m. p. 63-65°. yield 7 g. [Found : Cl, 14.1 (Shah's method, *J. Univ. Bombay*, 1936, 5, 62).  $C_{13}H_9$  NCl<sub>2</sub> requires Cl of imidochloride, 14.2 per cent].

The imidochloride can also be isolated by crystallising the residue obtained after distillation of phosphorus oxychloride under reduced pressure, from excess of petroleum ether. The imidochloride is readily soluble in common organic solvents. It was characterised by preparation of amidine derivative by the modified method of Shah (*J. Ind. Inst. Sci.*, 1924, 7, 219) as given below.

N : N'-Diphenyl-*p*-chlorobenzamidinc.—The imidochloride (2 g.) was slowly added to a mixture of diethylaniline (4 g.) and aniline (1.5 g.) and the whole heated in an oil bath at 130°-140° for 2 hours. The cooled reaction mixture was treated with dilute hydrochloric acid (1 : 1) so as to obtain the sparingly soluble hydrochloride which on trituration with ammonia and ethyl alcohol afforded the N : N'-diphenyl-*p*-chlorobenzamidine, crystallising from ethyl alcohol, m. p. 149°. (Found : N, 9.3. Calc. for  $C_{19}H_{15}N_2$  Cl : N, 9.1 per cent). Bharucha and Shah (*J. Univ. Bombay*, 1949, 17, v, 76) give m.p. 148-50°.

4-Hydroxy-2-*p*-chlorophenyl-3-acetylquinoline was prepared in 15% yield from *p*-chlorobenzanilide imidochloride as colorless needles. m. p. 284°. (Found: N, 5.1.  $C_{17}H_{12}O_2$  NCl requires N, 4.7 per cent ).

$\alpha$ -Naphthanilide imidochloride was prepared in the same way as *p*-chlorobenzanilide imidochloride from  $\alpha$ -naphthanilide ( 10 g. ) and phosphorus pentachloride (9. g.), m. p. 94-96°, yield 7.5 g. ( Found : Cl, 13.5.  $C_{17}H_{12}NCl$  requires Cl, 13.4 per cent ).

N : N'-Diphenyl- $\alpha$ -naphthamidine was prepared as above, m. p. 185°. Bosscheck ( *Ber.*, 1883, 16, 642 ) gives m. p. 183-85°.

4-Hydroxy-2- $\alpha$ -naphthyl-3-acetylquinoline was prepared in 15% yield from  $\alpha$ -naphthanilide imidochloride and crystallised from ethyl alcohol as tiny cream-coloured needles, m. p. 232-33°. ( Found : N, 4.7.  $C_{21}H_{15}O_2$  N requires N, 4.5 per cent ).

Methyl ether, m. p. 161-62° ( Found : N, 4.3.  $C_{22}H_{17}O_2$  N requires N, 4.3 per cent ).

4-Hydroxy-2- $\beta$ -naphthyl-3-acetylquinoline was prepared in 25% yield from  $\beta$ -naphthanilide imidochloride ( Shah and Chaubal, *loc. cit.* ), and crystallised from ethyl alcohol as colorless needles, m. p. 273-74°. ( Found : N, 4.6.  $C_{21}H_{15}O_2$  N requires N, 4.5 per cent ).

2:4-Dinitrophenylhydrazones, m. p. above 304°. ( Found : N, 13.9.  $C_{27}H_{17}O_5$  N<sub>5</sub> requires N, 14.1 per cent ).

The authors are grateful to Mr. P. L. Trivedi, M. Sc., for the analyses mentioned above.

ORGANIC CHEMISTRY LABORATORIES,  
ROYAL INSTITUTE OF SCIENCE,  
BOMBAY.

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## A STUDY ON THE VISCOSITY OF DECORTICATED TAMARIND SEED POWDER (*TAMARINDUS INDICA*, L.)

By D. B. DAS AND K. K. BASAK

Compared with other starches it has a higher initial viscosity and the rate of fall of viscosity on boiling is less. An explanation has been suggested for the change of viscosity of T. S. P. on boiling and it has been shown that the process is not exactly reversible. The lowering of the viscosity with increase in temperature has been discussed and an equation has been suggested for the relationship between viscosity and temperature. An equation has been suggested to represent the relationship between the viscosity of T. S. P. paste and its concentration. The effect of pH on the viscosity T. S. P. has been studied and it has been shown that the T.S.P. should be gelatinised in presence of  $M/1000$  sodium carbonate solution when the decrease of the viscosity of T. S. P. on boiling is almost completely arrested. A study on the effect of salt on viscosity shows that copper sulphate and zinc chloride should not be used with the T. S. P. size, but calcium chloride may be added. A probable explanation is given why the viscosity method may be accepted as a means of evaluating a starch for sizing. T. S. P. has been recommended to replace starch for jute warp sizing because of its cheapness and absence of food value.

High viscosity is a special physical property of high polymers. Another characteristic feature of the high polymeric substances is their ability to produce films of considerable tensile strength. It is likely that for a particular type of polymer, the higher its molecular weight, the stronger its film becomes, i. e. higher the viscosity, the greater is the strength of the film.

The best starches for sizing are those which can produce the strongest films on the warp yarns and it appears therefore that the valuation of a particular starch for sizing may be ascertained by measuring its viscosity. The viscosity method has therefore become of importance in assessing the quality of a starch and this method has been in use over a considerable period (Ermen, *J. Soc. Chem. Ind.*, 1907, 26, 501; MacNider, *Ind. Eng. Chem.*, 1917, 9, 597; Smith, *Text. Manuf.*, 1921, 47, 212). This method has also been adopted for the valuation of glue by Adhesive Research Committee (1st Report, 1922, p. 75, H. M. Stationery Office).

During the war years when the problem of supplies of starch for sizing became acute, tamarind seed powder was used largely in mills, especially in the Jute Industry and is being now used in continually increasing quantities. Some of the jute mills use other starches such as sago, maize, etc., of widely varying composition in the size mixture.

The purpose of the present work is mainly to investigate the physical properties of tamarind seed powder with special reference to viscosity and to ascertain if it can replace the other more conventional type of starches used in industry which are comparatively costly and difficult to obtain. Attempts have also been made in this paper to interpret the results in terms of molecular structure.

In the preparation of the size various substances are added for different purposes e. g. zinc chloride, copper sulphate, etc. are used as antiseptics ; sodium carbonate, caustic soda, borax, etc. for gelatinisation of starch, and so on. The present paper also deals with the effect of these reagents on the viscosity of tamarind seed powder.

The effects of the temperature, the time of boiling and the concentration of tamarind seed powder on the viscosity have also been studied and reported on.

### EXPERIMENTAL

Partly decorticated tamarind seed powder was sieved through a 3½ mesh sieve, the same sample being used throughout the whole investigation. It had an ash content of 2.55%. The sample was pale brown in colour, indicating the presence of a small amount of testa. The sago and maize had ash contents of 0.35% and 0.13% respectively.

*Preparation of the Pastes*—Preliminary investigations have shown that the viscosity of tamarind seed powder, like that of other starches, is dependent on the time of boiling of the paste. The paste was prepared by boiling a known quantity of the conditioned raw material with water or salt solution, as the case may be, for exactly 20 minutes, cooled, made to volume, strained through fine muslin and then used for the viscosity determinations. This concentration of the paste on dry weight was determined from its pre-determined moisture content. The paste was prepared in a glass beaker using a glass stirrer.

*Viscometer and the Measurement of the Viscosity*.—A British Standard Ostwald type viscometer (No. 2; Pamp. No. 188, 1929; British Standard Institution) was used in the usual way with the common precautions necessary for obtaining accurate values. For simplicity tamarind seed powder is referred to throughout this paper as 'T.S.P.' and relative viscosity as 'viscosity'.

### DISCUSSION

*Effect of Boiling*.—Viscosity of a starch paste usually falls with the time of boiling. As this property is of importance in evaluating the quality of a starch, the effect of boiling T. S. P. and different starches on the viscosity at 35° was studied. In these experiments attempts were made to choose the concentrations of the pastes in such a way that their initial viscosities were very near to one another. The results are summarised in Table I.

TABLE I

Time of boiling.	Relative viscosity		
	T. S. P. (0.5%)	Sago (1.0%)	Maize (1.5%)
10 mins.	4.7	5.2	4.9
20	5.0	4.0	4.6
30	4.3	3.3	4.5
60	3.8	2.9	4.0
180	2.9	2.8	2.7
300	2.5	2.5	2.4

It can be seen therefore that the T.S.P. has the highest initial viscosity and the effect of boiling on the viscosity of T.S.P. is the minimum. Again, in the case of T.S.P. there is an initial rise of viscosity to a maximum, followed by the usual fall. It is of course obvious that in all starch pastes this initial rise to a maximum due to the gelatinisation of the starch granules must take place, but usually the highest viscosity passes before any measurements are made.

A good deal of confusion has arisen in the past to attempt to explain changes of properties of solution by boiling until Wehr (*Kolloid Z.*, 1939, **88**, 185, 290) made a complete treatment of the subject. It is generally accepted that boiling causes the hydrolytic destruction of the chemical linkages in the originally existing starch paste. Tamarind seed powder consists of chains linked by gluco-galacto-xylan bonds (Savur and Sreenivasan, *J. Biol. Chem.*, 1948, 172, 501). On boiling it is probable that these bonds are hydrolysed, thereby causing the reduction of their molecular dimensions, and hence the viscosity.

*Effect of Temperature.*—As the temperature has a pronounced effect on the viscosity of a starch, the take-up of the size by the yarn depends greatly on the temperature of the size. Viscosity is relatively low at high temperatures and generally increases rapidly with decreasing temperature which results in a thicker paste. At a low temperature therefore the starch will set quickly on the yarn, give an uneven coating and dust off very rapidly. A comprehensive study of the effect of temperature on the viscosity of the 0.5% T.S.P. was therefore carried out. The results are shown in Table II and illustrated by Fig. 1.

TABLE II

Temp. of the sizes.	Relative viscosity of T. S. P.	
	Direct.	Reverse.
25°	6.8	6.1
35°	5.0	4.7
45°	3.8	3.6
60°	2.6	2.5
70°	2.1	2.0
75°	1.9	

The viscosity of tamarind seed powder also therefore increases rapidly with the decrease of temperature. Further, this change in the case of T.S.P. is not exactly reversible. This behaviour therefore cannot be explained only by the change of the molecular structure with the change of temperature. Hence the decrease in viscosity of T. S. P. at a higher temperature is partly due to the hydrolysis of the gluco-galacto-xylan bonds of T. S. P. molecules, and mainly due to their coiling at an elevated temperature.

Attempts were made to find a relationship between the viscosity of the T.S.P. and the temperature. Shinoda and Inagaki (*Cellulose Ind., Tokyo*, 1936, 12, 221) have found a temperature effect in the cellulose acetate in various solvents which could be expressed by a relationship of the type,

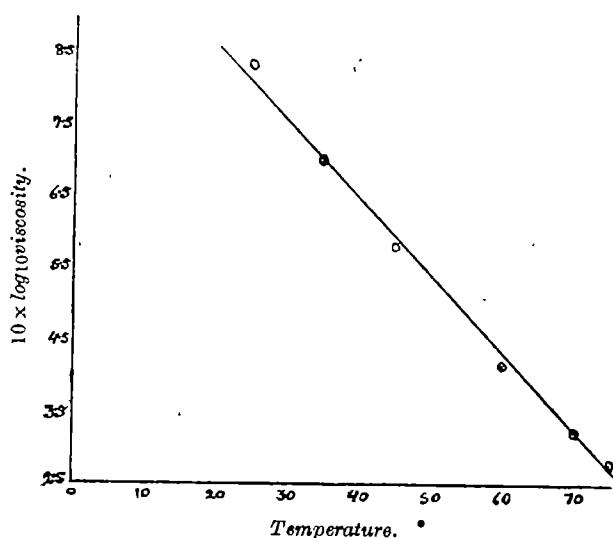
$$\eta_r = Ae^{-Bt}$$

where  $A$  and  $B$  are constants, and  $t$  is the temperature. This has been verified by other workers in the case of nitrocellulose in acetone.

Linear relationship between logarithm of the viscosity and the reciprocal of the temperature has been confirmed experimentally for many liquids. After a careful study of the above results, it is found from Fig. 1 that the temperature effect on the viscosity of the T. S. P. in water may approximately be represented by

$$\eta_r^{40^\circ} = e^{100-t}$$

FIG. 1



*Effect of Concentration.*—Viscosity of a starch paste increases with an increase of concentration. At higher concentrations this is greater than concentration increase. In the presence of 0.02%  $\text{Na}_2\text{CO}_3$  solution the increase of viscosity of T. S. P. at  $35^\circ$  with concentration is much more rapid than that in water, as shown in Table III, illustrated by Fig. 2.

TABLE III

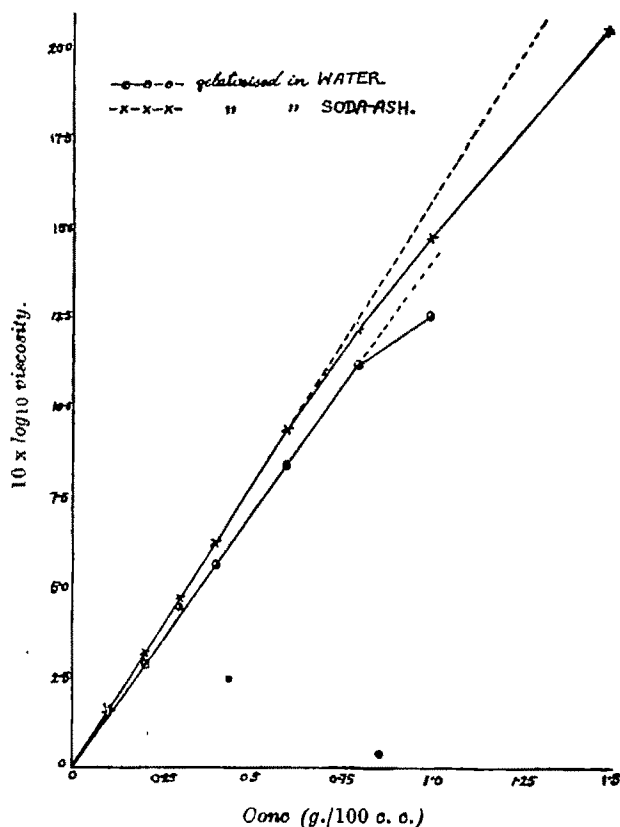
Conc. of T. S. P. (g./100 c. c., dry wt.)	Relative viscosity		$10 \times \log_{10}$ Relative viscosity.	
	Water.	$\text{Na}_2\text{CO}_3$ .	Water.	$\text{Na}_2\text{CO}_3$
0.1	1.5	1.4	1.6	1.6
0.1	1.9	2.1	2.9	3.2
0.3	2.8	3.0	4.4	4.7
0.4	3.7	4.2	5.6	6.2
0.6	6.9	8.7	8.4	9.4
0.8	13.1	16.6	11.2	12.2
1.0	17.9	29.4	12.5	14.7
1.5	--	111.5	--	20.5

Various equations have been proposed to correlate the viscosity of polymers with concentration. Arrhenius (*Z. physikal. Chem.*, 1887, 1, 285) suggested the following equation,

$$\log \eta_r = K. c.$$

Later on others (Bradée and Booy, *Kolloid Z.*, 1937, 79, 31, 43; Fikentscher, *Cellulose Chem.*, 1932, 13, 58; Papkow, *Kunststoffe*, 1935, 25, 253) also suggested similar equations. Several equations relating to the specific viscosity with concentration and intrinsic viscosity with concentration have also been proposed.

FIG. 2



Attempts were made to find a relation between the viscosity and the concentration of the T. S. powder. Various equations were tested and it is found that in dilute solution (up to the concentration of 0.8%) Arrhenius equation holds good (Fig. 2). Above this concentration, however, the log increases less rapidly with concentration increase. In dilute solution therefore the relationship between the viscosity of T. S. P. with water and concentration may be represented by

$$\log_{10} \eta_r = 1.4c.$$

*Effect of  $pH$ .*—Keeping the conditions of preparation of the starch paste and its concentration the same, it is obvious that the viscosity of tamarind seed powder will vary from  $pH$  to  $pH$ . Starches gelatinise generally in alkaline solution, and so it is anticipated that their viscosity will increase as the  $pH$  increases. On the other hand, alkalis cause degradation of starch and therefore it is to be expected that the viscosity of tamarind seed powder will reach a maximum and then decrease as the  $pH$  increases.

The effect of  $pH$  on the viscosity of 0.5% tamarind seed powder at  $35^\circ$  was therefore studied using citric acid-phosphate buffer, the results being shown in Table IV.

		TABLE IV				
$pH$		4	6	7	8	9.2*
Rel. viscosity		4.8	5.0	5.5	5.4	5.2

\* Unbuffered caustic soda solution.

If the data be plotted graphically it can be seen that the viscosity reaches a maximum at about  $pH$  7 and falls steeply on the acidic side and slowly on the alkaline side. The nature of the curve indicates that the maximum value probably lies in slightly alkaline solution.

It is well known that the viscosity of a polymer depends on the solvent.\*\* If the solvent is such that the attraction between the solvent and solute molecules is very great in comparison with the attraction between the solvent—solvent and the solute—solute molecules, the polymer molecules attain a more extended configuration, and hence an increase of viscosity with increase of  $pH$ , until neutral, may be explained as due to the uncoiling of the molecules at a higher  $pH$ . At a still higher  $pH$ , however, T. S. P. molecules suffer the breaking of gluco-galacto-xylan linkages to shorter chains, and hence the lowering of viscosity.

Control of the  $pH$  is of relatively minor importance for warp sizing, the whole character of the operation being determined by the higher initial viscosity and smaller change of viscosity with time. T. S. P. is therefore most suitable in dilute alkaline solution.

*Effect of Alkalis.*—As the above experiment shows that the viscosity increases in dilute alkaline solution, the effect of the concentration of the sodium carbonate, caustic soda and borax solutions on viscosity was studied to find the concentration of alkali required to give the maximum viscosity. The results are tabulated in Table V.

\*Here the term solvent means everything comprising the solution except the polymer.



TABLE V

Conc. of alkali.	Relative viscosity of T. S. P. in		
	Caustic soda,	Sodium carbonate,	Borax,
M/10	4.0	..	..
M/25	4.9	..	..
M/50	5.3	..	..
M/100	5.5	..	7.1
M/150	..	..	7.3
M/200	5.8	5.7	7.7
M/300	5.8	..	..
M/400	5.9	..	8.9
M/500	..	..	..
M/800	..	..	5.8
M/1000	6.3	6.4	7.2

T. S. P. for warp sizing should therefore be prepared in a very slightly alkaline solution when the maximum viscosity will be obtained. This is also supported by the fact that the rate of fall of viscosity at 35° on boiling is almost arrested in M/1000 sodium carbonate (Table VI), the pH of the paste being only 7-7.5. Even if the paste is kept 18 hours at room temperature, the viscosity drops to only 4.3 in comparison with that in water to 2.8. Strong alkaline solutions, however, cause degradation of T. S. P. and lowering of viscosity and should therefore be avoided.

TABLE VI

Time of boiling.	Relative viscosity of T. S. P. in	
	Water.	M/1000 Na <sub>2</sub> CO <sub>3</sub> .
10 mins.	4.7	5.7
20	5.0	6.1
30	4.3	6.3
60	3.8	6.4
180	2.9	5.9
300	2.5	5.7

*Effect of Salts.*—The addition of moderate quantities of soluble salts to a starch paste diminishes the viscosity (Richardson and Waite, *J. Text. Inst.*, 1933, 24, 383) in a manner similar to that which has been observed for sols and gum arabic (Taft and Malm, *J. Phys. Chem.*, 1931, 35, 874), for soluble starch (de Jong, *Rec. trav. chim.*, 1924, 43, 189) or agar (Kruij and de Jong, *Z. physikal. Chem.*, 1922, 100, 250). The fall of viscosity has been ascribed either to a diminution of hydration of the colloid brought about by the electrolyte, or to a diminution of its electrokinetic potential relative to water. As some of the salts, noted below, are used in jute sizing for different purposes, their effect on the viscosity of 0.5% T. S. P. at 35° has been studied and noted in Table VII.

TABLE VII

Salt.	Conc. of the salts.	Relative viscosity.
Nil	...	5.6
Zinc chloride	<i>M</i> /50	4.5
Calcium chloride	<i>M</i> /50	5.9
Copper sulphate	<i>M</i> /250	2.3

The addition of copper sulphate therefore causes considerable lowering of viscosity, whereas the addition of  $\text{CaCl}_2$  causes an increase in viscosity. Hence, if a high viscosity is aimed at, T.S.P. paste should be made up with very small amount of alkali and without the addition of copper sulphate or zinc chloride. Calcium chloride may, however, be added.

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## CERTAIN DERIVATIVES OF 4-AMINODIPHENYLSULPHONES

By U. P. BASU AND K. R. CHANDRAN

The preparation of certain acyl derivatives and Schiff's bases from 2 : 5-dihydroxy-4-amino- and -4-aminomethyldiphenylsulphone, as well as, from 2 : 4-dinitro-4'-aminodiphenylsulphone derivatives, has been described.

It is now generally believed that though the activity of common sulfa drugs depends to a considerable degree on the concentration of ionic form present in any condition, the drug action is brought about by combination of the drug through its basic amino group with some enzyme system of the organism (cf. Klotz, *J. Amer. Chem. Soc.*, 1944, 66, 459; Wood, *Brit. J. Exp. Path.*, 1940, 21, 74). It is difficult to approach the problem rationally as no definite knowledge on all enzyme systems of the micro-organism nor that of the host is yet known. The available evidence favours the view that a sulfa drug acts by displacement of *p*-aminobenzoic acid from an active centre in an enzyme surface, or, by simply competing with it for the formation of the enzyme complex. For this, presence of one free amino group would suffice, as even in sulphone groups the monoaminodiphenylsulphone derivatives are also being found to be active in comparison with diaminodiphenylsulphone (cf. Mingoia and Berti, *Chem. Abs.*, 1945, 39, 2057; Bauer, *J. Amer. Chem. Soc.*, 1948, 70, 2254; U. S. P. 2399600). Substitution of the amino group by a suitable grouping may again help in the isolation of a product that can acquire the property of forming an enzyme-drug complex at the site of infection. As a matter of fact, since the observations of Buttle (*Lancet*, 1937, p. 1331) and Fourneau (*Bull. Acad. Med.*, 1937, 110, 210) that *pp*-diaminodiphenylsulphone exerts a strong anti-streptococcal activity, several derivatives of the compound have been prepared which are found to be of promise even against leprosy and tuberculosis (Barry and McNalley, *Nature*, 1945, 156, 48; Cullomon and Raiziss, *Ann. Rev. Tuberc.*, 1946, 53, 374; Youmann *et al.*, *ibid.*, 1946, 54, 295; Brownlee, *Lancet*, 1948, *ii*, p. 131; Muir, *Trans. Roy. Soc. Trop. Med. Hyg.*, 1948, 41, 5, 575). Recently we also noticed (*Science & Culture*, 1949, 14, 339) that certain dihydroxyaminosulphones exhibit a bacteriostatic activity against *E. typhosa* and *V. Cholerae in vitro*. But this type of activity is completely unreliable guide for the discovery of compounds with activity *in vivo* (cf. Hoggarth and Martin, *Brit. J. Pharm. & Chem.*, 1948 3, 146). The chemistry of these and some

other new sulphone derivatives, since prepared, has, however, been recorded in the body of this paper.

#### EXPERIMENTAL

*Preparation of 4'-Acetaminodiphenylsulphones.*—To a hot solution of *p*-acetaminobenzene sulphinic acid ( "Org. Syntheses", Vol. V, p. 1 ) or *p*-acetaminomethylbenzene sulphinic acid ( cf. Sikdar and Basu, this *journal*, 1945, 22, 343 ) in water was added a molar amount of *p*-benzoquinone in water and the mixture was well shaken for half an hour and left aside. Crystals separating were crystallised from methyl alcohol ( cf. Buttle *et al.*, *Biochem. J.*, 1938, 32, 1101 ). Similarly a sodium salt solution of *p*-acetaminobenzene sulphinic acid in molar amount of 2 : 4-dinitrochlorobenzene in alcohol or refluxing for half an hour afforded the corresponding sulphone ( XI ).

*Hydrolysis to 4'-Aminosulphones.*—The acetyl derivative ( 1 part ) was heated under reflux with 17% hydrochloric acid ( 5 parts ) for 1 hour. The reaction mixture was cooled and neutralised with sodium carbonate. The solid separated was collected and crystallised from water in case of dihydroxy derivative ( I ) and from a mixture of acetone and alcohol ( 1 : 1 ) in case of the dinitro derivative ( X ). In case of the compound ( IV ) the reaction mixture was not neutralised, as hydrochloride on cooling separated out.

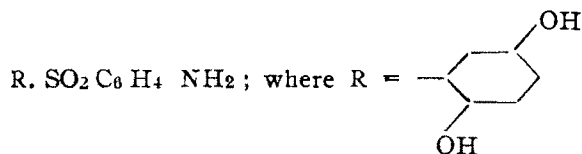
*Methylation of Dihydroxy Compounds.*—The acetaminohydroxy compounds were dissolved in sodium hydroxide solution ( 10% ) and the solution was treated with excess of dimethyl sulphate. The whole was refluxed for 1 hour on a water-bath. The reaction mixture was cooled and poured in ice water and the precipitate formed was collected and crystallised from alcohol. This on hydrolysis, as above, afforded the free aminosulphones ( III ) and ( VI ).

*Preparation of Cinnamoyl Derivatives ( VII ) and ( XII ).*—In the former case the aminosulphone ( I ) was dissolved in alcohol and in the latter, the compound ( X ) was dissolved in acetone, and the respective solution was refluxed for about 15 minutes. The cinnamoyl derivative separated was filtered and washed with alcohol.

*Preparation of Schiff's Bases*—In this case also, dihydroxysulphone ( I ) was dissolved in alcohol and dinitrosulphone ( X ) in acetone. The solution thus obtained was refluxed with cinnamic aldehyde ( 1.25 mole ) as well as with salicylaldehyde ( 1.25 mole ) for about 1 hour. In the former case, the anils ( VIII ) and ( IX ) separated on concentrating the alcoholic liquor and in the latter, the anils ( XIII ) and ( XIV ) were isolated by diluting the acetone solution with alcohol.

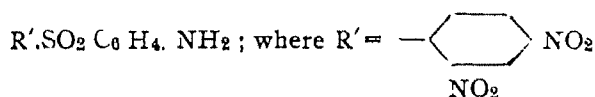
The characteristics of various compounds and derivatives, thus obtained, are recorded in Tables I and II.

TABLE I

*2:5-Dihydroxy-4-aminodiphenylsulphones*

Compound.	General character.	M. p.	Mol. formula and weight.	Nitrogen (%)	
				Found.	Calc.
(I) $R \cdot SO_2 \cdot C_6 H_4 \cdot NH_2$ OH = OMe	Colorless needles, insoluble in alkali.	165-66°	$C_{14}H_{15}O_4$ NS (293)	4.84	4.78
(II) $R \cdot SO_2 \cdot C_6 H_4 \cdot CH_2 \cdot NH_2$ HCl.	Colorless crystalline powder, soluble in alkali.	250-51° (decomp.)	$C_{13}H_{13}O_4$ NS HCl (315.5)	4.51	4.44
(III) $R \cdot SO_2 \cdot C_6 H_4 \cdot CH_2 \cdot NHAc$	Crystals from alcohol, soluble in alkali.	243-44°	$C_{15}H_{15}O_5$ NS (321)	4.65	4.34
(IV) $R \cdot SO_2 \cdot C_6 H_4 \cdot CH_2 \cdot NH_2$ OH = OMe	Needles from alcohol, insoluble in alkali.	275-76° (decomp.)	$C_{15}H_{17}O_4$ NS (307)	4.72	4.56
(V) $R \cdot SO_2 \cdot C_6 H_4 \cdot NH \cdot CO \cdot CH_3$ :CHPh	Colorless prisms, insoluble in common solvents but soluble in alkali.	297-98°	$C_{21}H_{17}O_5$ NS (395)	3.55	3.54
(VI) $R \cdot SO_2 \cdot C_6 H_4 \cdot N : CH \cdot CH :$ CHPh	Fine yellow needles, soluble in acetone and alkali.	216-17°	$C_{21}H_{17}O_4$ NS (379)	3.72	3.69
(VII) $R \cdot SO_2 \cdot C_6 H_4 \cdot N : CH \cdot C_6 H_4 \cdot OH$ (o)	Fine yellow-orange needles, soluble in acetone and alcohol.	235-36°	$C_{19}H_{15}O_5$ NS (369)	3.46	3.77

TABLE II

*2:4-Dinitro-4'-aminodiphenylsulphones*

Compounds.	General character.	M. p.	Mol. formula and weight	Nitrogen (%)	
				Found.	Calc.
(X) $R'.SO_2.C_6H_4.NH_2$	Orange crystalline substance, soluble in acetone but insoluble in alcohol.	220°	$C_{12}H_9O_6N_3S$ (323)	12.9	13.0
(XI) $R'.SO_2.C_6H_4.NHAc$	Needles with yellowish tinge, soluble in acetone.	231-32°	$C_{14}H_{11}O_7N_3S$ (365)	11.17	11.51
(XII) $R'.SO_2.C_6H_4.NH.CO.CH:$ CH.Ph	Pale yellow crystalline powder; slightly soluble in boiling acetone.	253-55°	$C_{21}H_{15}O_7N_3S$ (453)	9.35	9.27
(XIII) $R'.SO_2.C_6H_4.N:CH.CH:$ CH.Ph.	Red crystalline powder; soluble in acetone; sparingly in alcohol.	187-88°	$C_{21}H_{15}O_6N_3S$ (437)	9.16	9.6
(XIV) $R'.SO_2.C_6H_4.N:CH-$ $C_6H_4.OH(o)$	Yellow crystalline powder; soluble in acetone, sparingly in alcohol.	201-202°	$C_{19}H_{13}O_7N_3S$ (427)	9.54	9.83

BENGAL IMMUNITY RESEARCH INSTITUTE,  
CALCUTTA.

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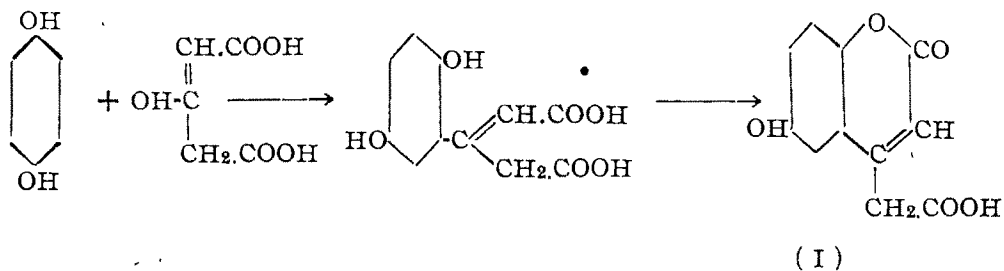
## SYNTHESIS OF 6-HYDROXYCOUMARIN-4-ACETIC ACID

By V. M. DIXIT AND V. U. PADUKONE

Quinol has been condensed for the first time with acetone dicarboxylic acid, and a fairly good yield of the condensation product viz., 6-hydroxycoumarin-4-acetic acid has been obtained. The identity of this compound has been established through some of its typical derivatives. The dimethyl ether of quinol has been condensed with acetone dicarboxylic acid under similar conditions, the product being 6-methoxycoumarin-4-acetic acid.

Quinol was found to react very feebly when Dey (*J. Chem. Soc.*, 1915, 107, 1606) tried to condense it with acetone dicarboxylic acid in the presence of sulphuric acid with a view to synthesising 6-hydroxycoumarin-4-acetic acid, and even when the acetone dicarboxylic acid was replaced by its diethyl ester, only a very small yield of the ethyl ester (m. p. 174-76°) of 6-hydroxycoumarin-4-acetic acid could be obtained. No reference could be found in literature to the preparation of the acid itself either by hydrolysis of this ester or by any other method of synthesis.

In the course of our investigation relating to the constitution of the  $\beta\beta$ -diaryl glutaric acids (*Proc. Indian Sci. Cong.*, 1948, Part III, p. 30) it was observed that quinol condensed easily with acetone dicarboxylic acid in the presence of 75% sulphuric acid according to the method described by Dixit and Gokhale (*J. Univ. Bom.*, 1934, 3, 80) and a fairly good yield (25%) of 6-hydroxycoumarin-4-acetic acid was obtained.



The other expected product, viz.,  $\beta\beta$ -di-2 : 5-dihydroxyphenylglutaric acid, however, could not be isolated.

The acid (I) was crystallised in silky white needles from hot water and melted at  $186^{\circ}$  with decomposition. It does not give a distinct coloration with  $\text{FeCl}_3$ . By decarboxylation at the melting point it changes to the known 6-hydroxy-4-methylcoumarin (m. p.  $245^{\circ}$ ) which gives an acetate (m. p.  $136^{\circ}$ ) (Pechmann and Boesche, *Ber.*, 1907, 40, 2731) and a benzoate (m. p.  $139^{\circ}$ ).

The acid (I) was also converted into its (i) acetate, m. p.  $183^{\circ}$  (decomp.), (ii) benzoate, m. p.  $220^{\circ}$ , (iii) methyl ester, m. p.  $172^{\circ}$ , and (iv) ethyl ester, m. p.  $180^{\circ}$ . The esters give a green coloration with  $\text{FeCl}_3$  in alcoholic solution. The acid (I) cannot be converted into 6-methoxycoumarin-4-acetic acid by ordinary methylation as it is found to be rather unstable in strong alkaline solutions which rapidly develop a dark colour on exposure. Hence, the above methoxy derivative (m. p.  $181^{\circ}$ , decomp.) was indirectly obtained in small quantity by condensing the dimethyl ether of quinol with acetone dicarboxylic acid in presence of 75% sulphuric acid. This condensation also did not yield the other expected products, viz. (i)  $\beta$ -2 : 5-dimethoxyphenylglutaconic acid, and (ii)  $\beta\beta$ -di-2 : 5-dimethoxyphenylglutaric acid.

## EXPERIMENTAL

**6-Hydroxycoumarin-4-acetic Acid.**—Anhydrous citric acid (50 g.) was heated with concentrated sulphuric acid (90 c. c.,  $d$  1.8) at  $60^{\circ}$ - $65^{\circ}$  till the effervescence of carbon monoxide subsided. The mixture was then cooled ( $5^{\circ}$ - $10^{\circ}$ ) and ice (10 g.) was gradually added to it with shaking without allowing the temperature to rise. Quinol (22 g.) was then added in small instalments and the mixture was kept overnight in a cool place. It was then poured on crushed ice (200 g.). The yellow granular solid which separated on stirring and scratching, was filtered, treated with a strong solution of sodium bicarbonate, the solution shaken with ether and then acidified with HCl. A white solid separated which crystallised from boiling water in silky needles, m. p.  $186^{\circ}$  (decomp.), yield 5 g. It formed an insoluble copper salt and gave a brownish coloration with  $\text{FeCl}_3$  in alcoholic solution. (Found: Equiv., 219; C, 59.82; H, 3.90.  $\text{C}_{11}\text{H}_8\text{O}_5$  requires equiv., 220; C, 60.0; H, 3.64 per cent).

**6-Acetoxy coumarin-4-acetic Acid.**—6-Hydroxycoumarin-4-acetic acid (1 g.) was refluxed with acetyl chloride (10 c. c.) on a water-bath for an hour. On pouring the mixture on ice a yellow liquid separated which solidified on keeping overnight. This crystallised from alcohol in silky needles, m. p.  $183^{\circ}$  (decomp.). yield 85%. (Found: Equiv., 261; C, 59.4; H, 3.88. Calc. for  $\text{C}_{13}\text{H}_{10}\text{O}_6$ : Equiv., 262; C, 59.54; H, 3.82 per cent).

**Benzoyl Derivative of 6-Hydroxycoumarin-4-acetic Acid.**—6-Hydroxycoumarin-4-acetic acid (1 g.) was dissolved in dry pyridine (10 c. c.) and benzoyl chloride (1 g.)



added in small quantities with shaking. The mixture was kept for 4 hours and poured in dilute (1:1) HCl. A small amount of a yellow solid separated on keeping overnight. It crystallised from dilute acetic acid in long prismatic needles, m. p. 220°, yield 20%. (Found: Equiv., 322; C, 66.46; H, 3.8. Calc. for  $C_{18}H_{12}O_6$ : Equiv., 324; C, 66.7; H, 3.7 per cent).

*Methyl Ester of 6-Hydroxycoumarin-4-acetic Acid.*—6-Hydroxycoumarin-4-acetic acid (1 g.) was dissolved in dry methyl alcohol (10 c. c.) and the solution was saturated with dry hydrochloric acid gas. On cooling the solution, the ester separated in yellowish needles, which crystallised from methyl alcohol in yellow needles, m. p. 172°, yield 90%. (Found: C, 61.4; H, 4.35. Calc. for  $C_{12}H_{10}O_5$ : C, 61.54; H, 4.27 per cent).

*Ethyl Ester of 6-Hydroxycoumarin-4-acetic Acid.*—It crystallised from alcohol in short yellowish needles, m. p. 180°, yield 1 g. (Found: C, 62.63; H, 5.22. Calc. for  $C_{13}H_{12}O_5$ : C, 62.90; H, 4.84 per cent).

*6-Hydroxy-4-methylcoumarin.*—6-Hydroxycoumarin-4-acetic acid (1 g.) was heated at its m. p. in a paraffin-bath until decarboxylation was complete. The resulting product was washed with a solution of sodium bicarbonate, and boiled with alcohol (animal charcoal). Yellowish prisms, m. p. 245°, yield 60%. (Found: C, 68.0; H, 4.75. Calc. for  $C_{10}H_8O_3$ : C, 68.2; H, 4.55 per cent).

*6-Acetoxy-4-methylcoumarin.*—6-Hydroxy-4-methylcoumarin (1 g.) was refluxed with acetyl chloride (8 c. c.) on a water-bath for one hour. On pouring the mixture in cold water a solid separated which was filtered, washed and crystallised from alcohol as white silky needles, m. p. 136°, yield 80%. (Found: C, 66.0; H, 4.8. Calc. for  $C_{12}H_{10}O_4$ : C, 66.06; H, 4.59 per cent).

*Benzoyl Derivative of 6-hydroxy-4-methylcoumarin* was prepared in a similar way as the benzoyl derivative of 6-hydroxycoumarin-4-acetic acid and obtained as a slightly crimson coloured solid which was filtered, washed with dilute hydrochloric acid and crystallised from dilute acetic acid as white shining needles, m. p. 139°, yield 1.1 g. (Found: C, 72.70; H, 4.63. Calc. for  $C_{17}H_{12}O_4$ : C, 72.85; H, 4.285 per cent).

*6-Methoxycoumarin-4-acetic Acid.*—Anhydrous citric acid (25 g.) was heated with concentrated sulphuric acid (45 c. c.,  $d$  1.8) until the elimination of carbon monoxide was complete. The mixture was cooled (5°-10°) and ice (10 g.) added carefully. Quinol dimethyl ether (12 g.) was added to it in small instalments with constant shaking. The shaking was continued for one hour and the reaction mixture was kept overnight at the room temperature. It was then poured on crushed ice (100 g.). On keeping overnight a small quantity of a yellowish powder separated.

It was filtered, washed several times with water and dissolved in sodium bicarbonate solution. The solution was shaken with ether and acidified with HCl. The solid which separated was filtered, washed and crystallised from boiling water in yellow shining needles, m. p,  $181^{\circ}$  (decomp.), yield 5%. ( Found : Equiv., 233.5. C, 61.69 ; H, 4.42. Calc. for  $C_{12}H_{10}O_5$  : Equiv., 234 ; C, 61.54 ; H, 4.27 per cent).

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DEPARTMENT OF CHEMISTRY,  
KARNATAK COLLEGE,  
DHARWAD.

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PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF COMPLEX  
METALLIC FERRO AND FERRICYANIDES. PART IX.  
CONDUCTOMETRIC AND THERMOMETRIC  
STUDIES ON THE COMPOSITION OF  
COPPER FERRICYANIDE

BY HARISH C. GAUR AND A. K. BHATTACHARYA

The composition of copper ferricyanide by the conductometric and thermometric titrations of copper sulphate and potassium ferricyanide has been studied. The titrations have been carried out in the aqueous and aqueous-alcoholic medium. The composition arrived at approximates to  $\text{Cu}_3(\text{Fe}^{\text{III}}\text{Cy}_6)_2$ .

AnalaR (B. D. H.) reagents were used for the preparation of the standard solutions of copper sulphate and potassium ferricyanide, which has been described in the previous communications (this *Journal*, 1947, 24, 487; 1948, 25, 349). Conductometric and thermometric titration arrangements were similar to those used previously (*loc. cit.*). Using different concentrations of the two salt solutions, the titrations were carried out by the direct and reverse methods, *i. e.*, when copper sulphate from the burette was added to potassium ferricyanide taken in the conductivity cell or the Dewar's flask, and *vice versa*. The titrations were also carried out in presence of alcohol up to a total concentration of 20% by volume.

M/5.0 solution of copper sulphate would be referred as A/1- $\text{CuSO}_4$  soln., and M/10 solution of potassium ferricyanide as A/1- $\text{K}_3\text{FeCy}_6$  soln.

TABLE I

Direct conductometric titrations.

(1) A/1- $\text{CuSO}_4$  and A/10- $\text{K}_3\text{FeCy}_6$ . Conc. ratio(n) = 10 : 1

A/10- $\text{K}_3\text{FeCy}_6$ in the cell.	Alcohol added	$\text{CuSO}_4$ soln. reqd. for 'v' c.c. $\text{K}_3\text{FeCy}_6$ in the cell.	$\text{CuSO}_4$ soln. calc. for 10 c.c. A/10- $\text{K}_3\text{FeCy}_6$ .	Equiv. vol of A/10- $\text{CuSO}_4$ .	Curve No.
(v)		( $v_1$ )	( $v_1/v$ ) $\times$ 10	n ( $v_1/v$ ) $\times$ 10	
10 c.c.	0.0 c.c.	1.50 c.c.	1.50 c.c.	15.00 c.c.	1
9	1.0	1.34	1.49	14.88	2
8	2.0	1.18	1.475	14.75	3

TABLE I (Contd.)

*Reverse conductometric titrations.*(ii) A/2-K<sub>3</sub>FeCy<sub>6</sub> and A/10-CuSO<sub>4</sub>.

Conc. ratio(n) = 5 : 1.

A/10-CuSO <sub>4</sub> in the cell. (v)	Alcohol added.	K <sub>3</sub> FeCy <sub>6</sub> reqd. for 'v' c.c. CuSO <sub>4</sub> in the cell. (v <sub>1</sub> )	K <sub>3</sub> FeCy <sub>6</sub> calc. for 10 c.c. A/10-CuSO <sub>4</sub> (v <sub>1</sub> /v) × 10	Equiv. vol. of A/10- K <sub>3</sub> FeCy <sub>6</sub> n(v <sub>1</sub> /v) × 10	Curve No.
10 c.c.	0.0 c.c.	1.29 c.c.	1.29 c.c.	6.45 c.c.	4
9.0	1.0	1.18	1.31	6.55	5
8.0	2.0	1.07	1.35	6.65	6

(in) A/4-K<sub>3</sub>FeCy<sub>6</sub> and A/10-CuSO<sub>4</sub>.

Conc. ratio(n) = 2.5 : 1.

10 c.c.	0.0 c.c.	2.60 c.c.	2.60 c.c.	6.50 c.c.	7
9.0	1.0	2.38	2.644	6.61	8
8.0	2.0	2.12	2.65	6.62	9

TABLE II

*Direct thermometric titrations.*(i) A/2-CuSO<sub>4</sub> and A/10-K<sub>3</sub>FeCy<sub>6</sub>.

Conc. ratio(n) = 5 : 1.

A/10-K <sub>3</sub> FeCy <sub>6</sub> in the cell. (v)	Alcohol added.	CuSO <sub>4</sub> reqd. for 'v' c.c. A/10-K <sub>3</sub> FeCy <sub>6</sub> in thermoflask. (v <sub>1</sub> )	CuSO <sub>4</sub> calc. for 20 c.c. A/10-K <sub>3</sub> FeCy <sub>6</sub> (v <sub>1</sub> /v) × 20	Equiv. vol. of A/10-CuSO <sub>4</sub> . n(v <sub>1</sub> /v) × 20	Curve No.
20 c.c.	0.0 c.c.	6.0 c.c.	6.00 c.c.	30.0 c.c.	10
18	2.0	5.35	5.94	29.72	11
16	4.0	4.65	5.81	29.05	12

(ii) A/4-CuSO<sub>4</sub> and A/10-K<sub>3</sub>FeCy<sub>6</sub>

Conc. ratio(n) = 2.5 : 1.

20 c.c.	0.0 c.c.	11.95 c.c.	11.95 c.c.	29.9 c.c.	13
18	2.0	10.70	11.89	29.7	14
16	4.0	9.40	11.75	29.4	15

TABLE II ( *Contd.* )*Reverse thermometric titrations*( i ) A/10- $K_3FeCy_6$  and A/10- $CuSO_4$ . Conc. ratio(n) = 2.5 : 1.

A/10- $CuSO_4$ in thermos flask. ( v )	Alcohol added.	$K_3FeCy_6$ reqd. for 'v' c.c. $CuSO_4$ in the thermos flask. ( v <sub>1</sub> )	$K_3FeCy_6$ calc. for 20 c.c. A/10- $CuSO_4$ ( v <sub>1</sub> / v ) × 20	Equiv. vol. of A/10- $K_3FeCy_6$ n ( v <sub>1</sub> / v ) × 20	Curve No.
20 c.c.	0.0 c.c.	5.20 c.c.	5.20 c.c.	13.00 c.c.	16
18	2.0	4.75	5.28	13.20	17
16	4.0	4.30	5.37	13.42	18

( ii ) A/4- $K_3FeCy_6$  and A/4- $CuSO_4$ . Conc. ratio(n) = 1 : 1.

20 c.c.	0.0 c.c.	13.0 c.c.	13.0 c.c.	13.0 c.c.	19
18	2.0	11.9	13.22	13.22	20
16	4.0	10.8	13.50	13.50	21

## DISCUSSION

From the strengths of the solutions of copper sulphate ( M/5.0 ) and potassium ferricyanide [ M/5.1 ], the calculated titre values for the formation of the more probable compounds are given in Table III.

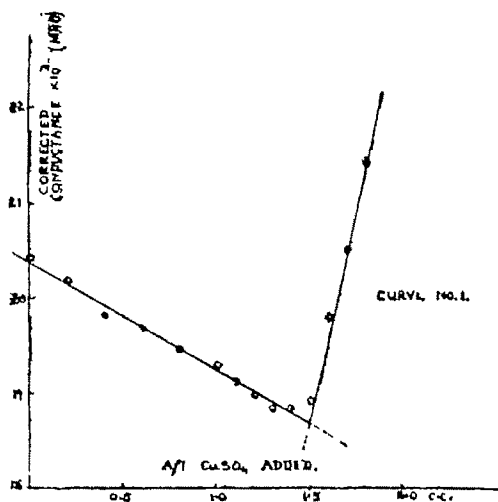
TABLE III

Formulae.	$KCuFe^{III}Cy_6$	$Cu_2(Fe^{III}Cy_6)_2$
1. Titre value of $CuSO_4$ for 10 c.c. of $K_3FeCy_6$ soln. in the direct titrations ...	9.8 c.c.	14.70 c.c.
2. Titre value of $K_3FeCy_6$ for 10 c.c. of $CuSO_4$ soln. in the reverse titrations ...	10.2	6.8

Comparing these with the titre values obtained by the conductometric and thermometric titrations ( Table I and II ), it is obvious that both in the direct and reverse titrations the molecular composition of copper ferricyanide corresponds to  $Cu_2[Fe^{III}Cy_6]_2$ .

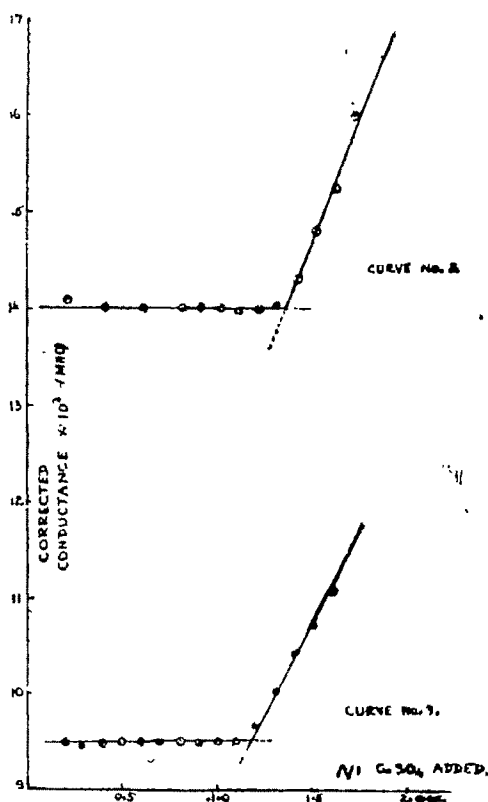
In the case of direct titrations (copper sulphate added to potassium ferricyanide), the observed titre values of copper sulphate (15.0 c.c.) in aqueous medium for 10 c.c. of potassium ferricyanide solution is higher than the calculated value (14.70 c.c.); while in the case of reverse titrations ( $K_3FeCy_6$  added to copper sulphate) the observed titre values of potassium ferricyanide (6.45 to 6.5 c.c.) for 10 c.c. of copper sulphate in aqueous medium are lower than the calculated value (6.80 c.c.) for

FIG. 1



the formation of the compound  $\text{Cu}_3(\text{Fe}^{\text{III}}\text{Cy}_6)_2$ . When the titrations are carried out in presence of increasing amounts of alcohol, the observed titre values both in the case of direct and reverse titrations approach the calculated titre values more closely.

FIG. 2



The discrepancy between the observed and the calculated titre values, (in direct and reverse titrations) in aqueous medium, and the subsequent change when the titrations are performed in aqueous-alcoholic medium, supports our view on hydrolytic and adsorptive nature of such complexes (cf. Parts I to VIII, this *Journal*).

On hydrolysis copper ferricyanide would release some  $\text{FeCy}_6^{\text{III}}$  which will consume some extra amount of copper sulphate, though a little it may be, hence the amount of copper sulphate required will be slightly greater than the calculated equivalent when

the titrations are carried out in aqueous medium by the direct process (copper sulphate added to potassium ferricyanide). And conversely in reverse titrations, a slight decrease in the titre value from the calculated equivalent will be observed when the titrations are performed in aqueous medium. In presence of alcohol the hydrolysis is checked to some extent, and thus the observed titre values both in the case of direct and reverse titrations approach the calculated ones more closely.

FIG. 3

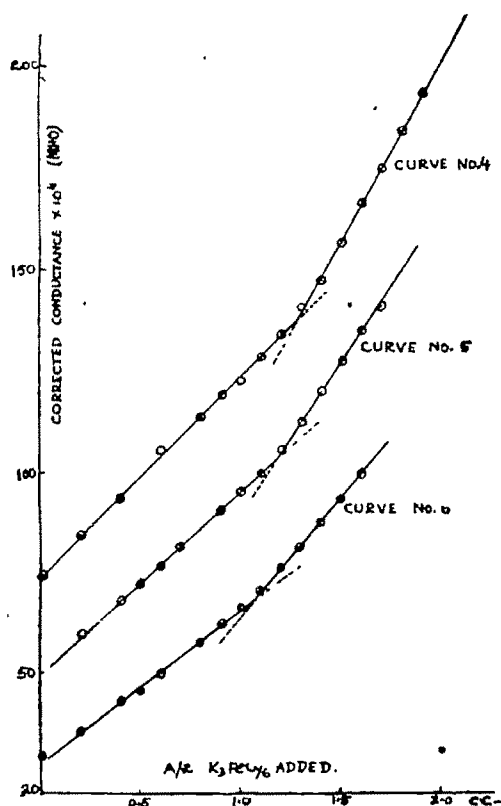
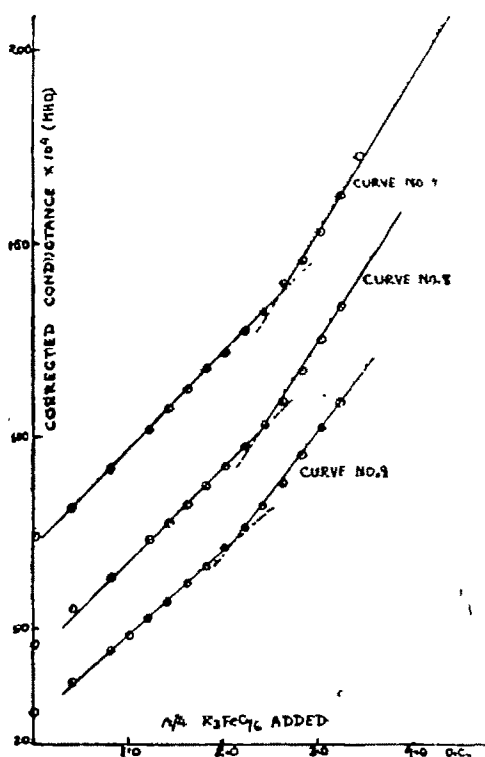


FIG. 4



The absorption of  $Cu^{++}$  and  $FeCy_6^{III}$  ions by the precipitated copper ferricyanide may also bring about this discrepancy. In the case of direct titrations ( $CuSO_4$  added to  $K_3FeCy_6$ ) the precipitate is gradually formed in presence of  $FeCy_6^{III}$  ions and the chances of absorption of these ions will be greater. In the case of reverse titrations ( $K_3FeCy_6$  added to  $CuSO_4$ ) on the other hand, the precipitate is formed in the medium of  $Cu^{++}$ , and hence it is likely that these ions will be absorbed more in this case. On this consideration the observed titre values both in the case of direct and reverse titrations would be lower than the calculated one for the formation of the probable

compound. This quite explains the lower observed value than the calculated one in the case of reverse titrations. But in the case of direct titrations the observed titre values of copper sulphate for 10 c.c. of potassium ferricyanide in aqueous medium are higher than the calculated one. This abnormality may be explained on the basis of the absorption experiments that have been carried out. Quantitative experiments have shown that copper ferricyanide sol absorbs  $\text{Cu}^{++}$  ions to a much greater extent than  $\text{FeCy}_6^{+++}$  ions. For the same value of equilibrium concentration (4.69 g./litre), the values of  $x/m$  for  $\text{FeCy}_6^{+++}$  and  $\text{Cu}^{++}$  ions have been found to be 0.14 and 0.70 m/moles respectively. Hence it appears that the sum total effect of the absorbed  $\text{Cu}^{++}$  and hydrolysis is greater than the loss of  $\text{FeCy}_6^{+++}$  due to its absorption by the precipitated complex in the cell. Hence the titre from the burette will be higher.

FIG. 5

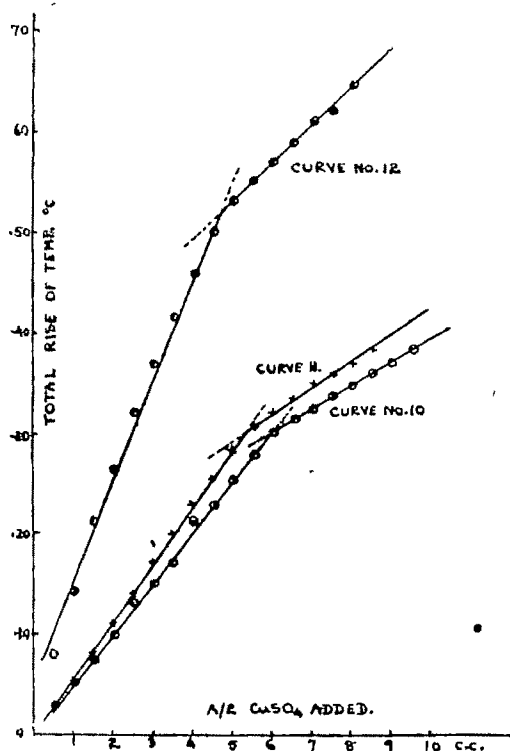
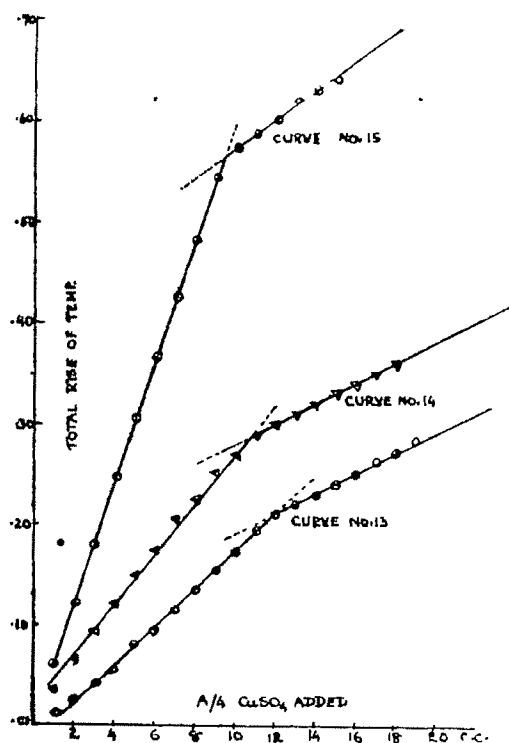


FIG. 6



Thus the apparent discrepancy between the titre values as obtained by the thermometric and the conductometric methods, and those calculated on the basis of the strengths of the reacting solutions may be accounted for. In fact, it is difficult to account for the discrepancy by considering only one of these effects singly without considering the simultaneous effect of the other.



FIG. 7

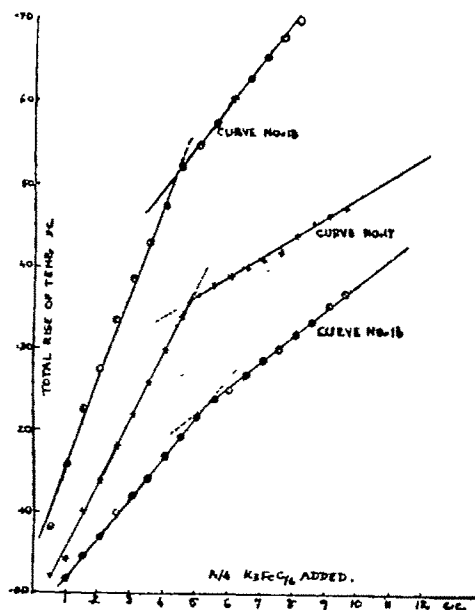
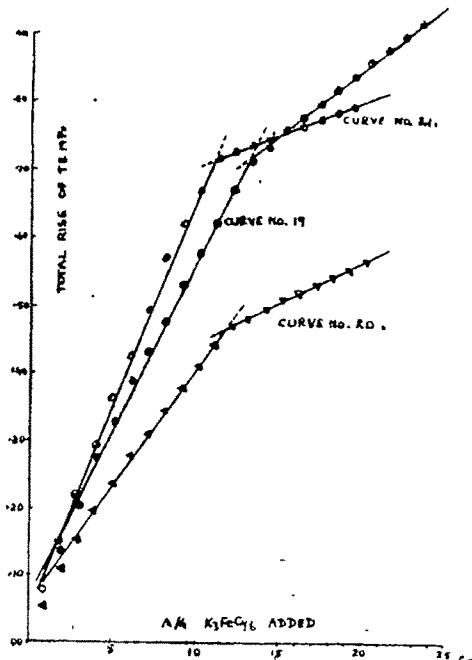


FIG. 8



Quantitative absorption of  $Cu^{++}$  and  $FeCye^{III}$  ions by copper ferricyanide sol, and the hydrolysis of the sol have been studied. The results will follow shortly.

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DEPARTMENT OF PHYSICAL CHEMISTRY,  
AGRA COLLEGE, AGRA.

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# VARIATION OF RELATIVE VISCOSITY WITH TEMPERATURE. NON-AQUEOUS SOLUTIONS OF ELECTROLYTES AND NON-ELECTROLYTES

BY A. C. CHATTERJI AND A. N. BOSK

The variation of relative viscosity with temperature has been studied. It has been observed that the value of  $\frac{\delta}{\delta t} \left( \eta_r / \eta_o \right)$  is negative for all the solutions studied here.

In previous communications (this *Journal*, 1948, 25, 93; 1949, 26, 91) the variation of relative viscosity with temperature has been studied. In the present paper the work has been extended to a few more solutions of electrolytes and non-electrolytes in non-aqueous solvents.

Experimental method used is the same as given in the previous communications (*loc. cit.*). Results obtained are given in Table I. Concentrations are given in g. of solute per 100 g. of solvent.

TABLE I

Solute.	Conc.	30°.	35°.	40°.	45°.
	Solvent=Acetone.				
1. Benzoic acid	50.0	2.218	2.174	2.144	2.146
	60.0	2.455	2.405	2.353	2.303
2. Salicylic acid	45.5	2.093	2.046	2.015	2.020
	54.5	2.443	2.354	2.322	2.305
3. <i>o</i> -Nitrobenzoic acid	67.9	3.428	3.327	3.258	3.200
	81.2	4.708	4.578	4.441	4.325
4. Phthalic acid	5.2	1.183	1.179	1.161	1.177
5. Cinnamic acid	20.4	1.617	1.605	1.581	1.592
6. <i>m</i> -Nitrobenzoic acid	59.9	2.953	2.898	2.838	2.826
	103.5	5.614	5.312	5.203	5.058
7. Oxalic acid	11.8	1.472	1.459	1.453	1.452
	32.4	2.876	2.807	2.726	2.691

TABLE I ( *contd.* )

Solute.	Conc.	35°.	40°.	45°.	50°.
Solvent=Methyl alcohol.					
8. KI	10.0	1.261	1.250	1.248	1.251
	20.0		1.459	1.453	1.448
9. NH <sub>4</sub> Br	5.33	1.280	1.275	1.260	1.264
	12.85	1.539	1.536	1.512	1.525
10. NH <sub>4</sub> NO <sub>3</sub>	19.60	1.880	1.862	1.852	1.856
	27.30		2.315	2.102	2.101
11. KCNS	23.70	1.964	1.942	1.910	1.907
	31.20	2.310	2.241	2.209	2.172
12. NH <sub>4</sub> CNS	2.580	1.972	1.996	1.954	1.953
	3.580	2.315	2.308	2.280	2.280
Solvent = Propyl alcohol.					
13. NaI	20.01	1.605	1.594	1.575	1.552
	29.70	1.978	1.973	1.957	1.938
14. KCNS	4.32	1.132	1.270	1.321	1.222
	6.01	1.206	1.200	1.206	1.191

## DISCUSSION

It may be observed that in case of all the solutions  $\frac{\delta}{\delta t} \left( \eta_s / \eta_0 \right)$  is negative. So far as the acetone solutions are concerned the results are according to our expectations ( Chatterji and Ram Gopal, this *Journal*, 1947, 24, 455 ) as both the solvent and solute are polar and the solvates formed by their combination are expected to break with rise of temperature. Solutions of electrolytes in methyl and propyl alcohols are expected to gain positive values for  $\frac{\delta}{\delta t} \left( \eta_s / \eta_0 \right)$  due to the depolymerising effect of the solute molecules, but they too have given negative values. Similar results have been obtained by Briscoe and Reinhart (*J. Phys. Chem.*, 1942, 46, 387) in their study of solutions of potassium iodide in methyl alcohol. Probably the unexpected behaviour is due to the high concentration of the solutions studied.

## THE VARIATION OF SPECIFIC CONDUCTIVITY WITH CONCENTRATION OF WEAK ELECTROLYTES IN NON-AQUEOUS SOLVENTS

By A. C. CHATTERJI AND A. N. BOSH

The variations of specific conductivity of weak electrolytes with concentration has been studied in non-aqueous solvents. It has been observed that the solutions can be divided into two categories :

( i ) The solutions which give a straight line plot or nearly so for  $\mu - c$  within the concentration range studied here.

( ii ) The plot of  $\mu - c$  shows a maximum. In some cases the first concentration of the solute is so high that further addition of the solute diminishes the conductivity.

It has been suggested that if the relative increase in the viscosity is more than the relative increase in the specific conductivity with increasing concentration then a maximum is obtained in the plot of  $\mu - c$ .

The variation of specific conductivity with concentration of the aqueous solutions of electrolytes has been studied by several workers. Jones, Blitz and their collaborators ( Jones, "Hydrates in Aqueous Solutions", 1907, pp. 840, 907 ) measured the conductivity of aqueous solutions of  $\text{CoCl}_2$  and  $\text{CuCl}_2$  in presence of various dehydrating agents and noticed a maximum in the plot of  $\mu - c$  and suggested that it was due to the increase in the viscosity of the solutions. Usanovitsch ( *J. Gen. Chem. USSR.*, 1940, 10, 59 ) pointed out that the maximum in the  $\mu - c$  curve was either due to complex formation or due to opposing forces of viscosity and concentration.

Ram Gopal ( Thesis, Lucknow University, 1946 ) studied the variation of specific conductivity with concentration for supersaturated aqueous solutions and pointed out that the solutions could be divided into two categories. In category one belong the substances which have very little hydrating power and hence a lower viscosity. Substances of the second category pass through a maximum at ordinary concentrations.

From the above consideration it appears that practically no work has been done on the variation of specific conductivity with concentration for the non-aqueous solutions of weak electrolytes, especially when highly concentrated and supersaturated solutions are taken.

Experimental method followed is the same as given in a previous communication ( this issue, p. 138 ). The results obtained are given in Table I.

TABLE I

*The variation of specific conductivity with concentration.*

Concentration is given in g. of solute per 100 g. of solvent.

Solute.	Temp.	Solvent = Acetone.					
Benzoic acid	35° 45°	$\kappa =$	52.54 7.420 8.010	59.44 7.095 7.781	66.97 6.873 7.571	72.41 6.541 7.201	$\times 10^{-7}$
Salicylic acid	30° 45°	$\kappa =$	48.47 1.752 1.982	56.42 1.772 2.033	63.73 1.765 2.037	70.33 1.765 2.066	$\times 10^{-6}$
<i>o</i> -Nitrobenzoic acid	25° 45°	$\kappa =$	74.01 4.578 6.053	81.91 4.456 5.940	106.10 4.190 5.624	113.00 3.908 5.256	$\times 10^{-6}$
<i>m</i> -Nitrobenzoic acid	25° 45°	$\kappa =$	50.22 1.713 2.118	59.75 1.758 2.214	79.95 1.796 2.320	90.60 1.809 2.390	$\times 10^{-6}$
<i>o</i> -Aminobenzoic acid	25° 45°	$\kappa =$	22.20 1.689 2.033	32.40 2.778 3.431	70.50 4.365 5.570	89.10 4.922 6.440	$\times 10^{-6}$
Cinnamic acid	30° 45°	$\kappa =$	19.26 7.683 8.754	32.92 9.430 11.190	38.65 9.772 11.190	44.16 9.798 11.136	$\times 10^{-7}$
Phthalic acid	30° 45°	$\kappa =$	1.705 5.723 6.410	3.490 6.836 7.381	5.354 7.421 8.221	6.473 8.716 9.832	$\times 10^{-7}$
Oxalic acid	25° 45°	$\kappa =$	4.504 4.220 4.778	12.49 8.664 10.300	24.74 14.580 18.290	32.16 18.130 23.470	$\times 10^{-5}$
Succinic acid	35° 45°	$\kappa =$	1.826 1.604 1.657	3.264 2.566 2.671	5.110 3.388 3.562	6.868 4.148 4.393	$\times 10^{-5}$
Solvent = Methyl alcohol.							
Benzoic acid	35° 45°	$\kappa =$	72.21 4.689 5.447	77.63 4.393 5.156	82.55 4.276 4.933	90.55 3.981 4.652	$\times 10^{-6}$
Salicylic acid	30° 45°	$\kappa =$	52.97 3.470 4.393	58.78 3.392 4.310	64.36 3.310 4.280	68.74 3.271 4.172	$\times 10^{-6}$
<i>o</i> -Nitrobenzoic acid	25° 45°	$\kappa =$	57.24 4.578 6.053	81.91 4.456 5.940	106.10 4.190 5.624	113.00 3.908 5.256	$\times 10^{-6}$
<i>m</i> -Nitrobenzoic acid	25° 45°	$\kappa =$	28.66 1.526 2.178	55.50 1.570 2.270	73.03 1.456 2.172	89.24 1.362 2.042	$\times 10^{-5}$
<i>o</i> -Aminobenzoic acid	35° 45°	$\kappa =$	35.81 5.845 6.247	42.45 6.247 6.543	53.65 6.533 6.983	60.42 6.627 7.080	$\times 10^{-5}$

TABLE I ( contd. )

Solute.	Temp.	Solvent=Methyl alcohol.						
Cinnamic acid	25° 45°	$c=$	10.22 0.9268 1.228	26.76 0.8537 1.151	33.54 0.8018 1.152	40.40 0.7390 1.018	$\times 10^{-5}$	
Phthalic acid	30° 45°	$c=$	19.48 4.539 6.290	27.81 4.677 6.540	34.43 4.617 6.540	44.40 --- 6.306	$\times 10^{-5}$	
Solvent=Propyl alcohol.								
Benzoic acid	30° 45°	$c=$	24.10 2.198 2.761	32.53 2.034 2.554	43.03 1.918 2.424	58.11 1.789 2.236	65.40 1.599 1.918	$\times 10^{-7}$
<i>m</i> -Nitrobenzoic acid	30° 45°	$c=$	60.93 1.622 2.248	70.55 1.581 2.233	83.90 1.381 2.170	94.74 1.497 2.154	114.5 1.375 2.038	$\times 10^{-7}$
Cinnamic acid	30° 45°	$c=$	11.05 5.624 7.093	22.19 6.511 8.280	28.50 6.486 8.461	33.15 6.410 8.461	$\times 10^{-7}$	
Phthalic acid	25° 45°	$c=$	5.05 2.387 3.758	7.25 2.697 4.273	9.21 2.938 4.626	11.00 3.182 5.017	$\times 10^{-6}$	
Succinic acid	25° 45°	$c=$	1.945 3.294 4.933	3.174 4.919 7.287	4.922 6.610 9.726	8.468 9.004 13.080	9.480 9.726 14.090	$\times 10^{-6}$
Oxalic acid	35° 45°	$c=$	16.03 9.330 9.816	28.45 23.990 25.710	44.30 44.640 47.940	57.34 61.140 65.940	61.87 --- 70.550	$\times 10^{-5}$
Solvent= <i>n</i> -Butyl alcohol.								
Salicylic acid	35° 45°	$c=$	18.62 6.255 7.955	22.72 7.075 8.786	17.72 7.428 9.080	38.25 7.947 9.853	$\times 10^{-7}$	
<i>o</i> -Nitrobenzoic acid	25° 45°	$c=$	11.90 5.991 7.665	20.77 7.755 9.970	30.94 9.440 12.050	46.93 10.400 14.380	$\times 10^{-7}$	
<i>o</i> -Aminobenzoic acid	25° 45°	$c=$	4.35 1.724 2.390	12.10 2.630 3.384	18.10 2.981 3.923	22.00 3.298 4.270	26.14 --- 4.344	$\times 10^{-7}$
Succinic acid	35° 59°	$c=$	1.150 1.463 1.854	2.620 2.671 3.295	3.728 3.452 4.191	5.609 4.337 5.239	$\times 10^{-6}$	
Phthalic acid	35° 45°	$c=$	2.266 1.009 1.199	4.256 1.385 1.619	6.714 1.713 2.043	10.600 1.828 2.324	$\times 10^{-6}$	

NOTE : (1) Specific conductivity has been determined at five different temperatures but due to brevity of space it is given at two different temperatures.

(2) 'c' denotes the concentration in g. of solute per 100 g. of solvent.

## D I S C U S S I O N

From the results given in Table I specific conductivity has been plotted against concentration. The results for the plot of  $\mu \cdot c$  can be divided into two categories :

( i ) Those that give a straight line plot or nearly so, e. g. solutions of oxalic and phthalic acid in propyl alcohol and oxalic acid in acetone.

( ii ) Those that pass through a maximum, e. g. solutions of benzoic acid in methyl and propyl alcohols, *o*-aminobenzoic acid in butyl alcohol, etc. In some cases the concentration of the solute is so high that further addition of the solute diminishes the conductivity, e. g. in solutions of cinnamic acid and *o*-nitrobenzoic acid in methyl alcohol, etc.

Solutions of the second type show a maximum probably due to the fact that as the concentration increases, the viscosity increases, but if the relative increase in the viscosity is more than the relative increase in the conductivity then the plot of  $\mu \cdot c$  should pass through a maximum ; whereas in those solutions in which a straight line plot is obtained, the above two increases are proportional to the increase in concentration.

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CHEMICAL LABORATORIES, THE UNIVERSITY,  
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## THE VARIATION OF SPECIFIC CONDUCTIVITY WITH TEMPERATURE OF NON-AQUEOUS SOLUTIONS OF WEAK ELECTROLYTES

By A. C. CHATTERJI AND A. N. BOSCH

The variation of specific conductivity with temperature has been studied. It has been observed that for the solutions of different organic acids in methyl alcohol, the plot of  $\mu \cdot t$  is a straight line. But for a few solutions where the viscosity is high the plot of  $\mu \cdot t$  is not a straight line and therefore these solutions do not obey Walden's equation (1) and probably these solutions obey the equation of Kohlrausch (2). Solutions of butyl and propyl alcohols and acetone obey the equation (1) where the conductivity is high, otherwise they obey the equation (2). It has been observed that in the case of substituted benzoic acids the conductivity of the substituted compound follows the order:  $\text{NH}_2 > \text{NO}_2 > \text{OH}$  group.

Variation of molecular conductivity of organic acids in ethyl alcohol with temperature has been studied by Wiesel, Jones and Wightman (*J. Amer. Chem. Soc.*, 1914, **36**, 2243). Hunt and Briscoe (*J. Phys. Chem.*, 1929, **33**, 1495) found several interesting results regarding the structure of the acid and the conductivity in the case of solutions of various substituted benzoic acids in ethyl alcohol. In the present paper the variation of specific conductivity with temperature of the solutions of weak electrolytes in methyl, propyl and butyl alcohols and acetone has been studied and the validity of the equations of Walden and Kohlrausch has been tested. Molecular conductivity of the solutions could not be determined as the solutions taken were highly concentrated and supersaturated, and hence density could not be accurately determined.

### EXPERIMENTAL

All the solutes and the solvents from Kahlbaum and B. D. H. were purified by the standard methods and the solutes were dried in a vacuum desiccator.

We have used the Kohlrausch bridge assembly consisting of a calibrated straight bridge wire, tunable headphone and an audio-oscillator consisting of a tuning fork giving a constant frequency of 1000 cycles per second and which can be worked by a six volt battery.

Air condenser, the capacity of which could be varied, was used for balancing the capacities and inductions in the various arms as well as in the resistances in the bridge, to overcome electrode effect and to aid in producing a definite and easily determined minimum sound in the telephone.



The cell constant was found to be 0.02720 and did not vary with temperatures. The cell constant was checked from time to time.

Bhattacharya and Nakhate's ( this *Journal*, 1947, 24, 1, 99 ) method was followed in preparing the solutions.

Results obtained are given in Table I.

TABLE I

*The variation of specific conductivity with temperature.*

Solute.	Conc. ( g./100 g. )	25°.	30°.	35°.	40°.	45°.	
Solvent = Acetone.							
Benzoic acid	52.54 72.41	6.762	7.074	7.420 6.541	7.781 6.931	8.010 7.201	} $\times 10^{-7}$
Salicylic acid	48.47 70.33	1.651	1.752 1.765	1.823 1.855	1.914 1.962	1.982 2.066	} $\times 10^{-6}$
<i>o</i> -Nitrobenzoic acid	74.01 113.00	4.578 3.908	4.936 4.211	5.313 4.594	5.675 4.922	6.053 5.256	} $\times 10^{-6}$
<i>m</i> -Nitrobenzoic acid	50.22 98.91	1.713 1.747	1.822 1.963	1.932 2.095	2.031 2.230	2.118 2.406	} $\times 10^{-6}$
<i>o</i> -Aminobenzoic acid	70.50 101.20	4.365 5.450	4.698 5.794	4.930 6.043	5.310 6.550	5.570 6.948	} $\times 10^{-6}$
Cinnamic acid	38.65 48.78		9.772	10.320	10.800 10.960	11.190 11.500	} $\times 10^{-7}$
Phthalic acid	6.47 7.33		8.716 14.640	9.142 15.240	9.575 15.790	9.832 16.490	} $\times 10^{-6}$
Oxalic acid	32.16 38.56	18.130 21.150	19.370 22.820	20.810 24.700	22.140 26.500	23.470 28.070	} $\times 10^{-5}$
Succinic acid	3.27 6.868	2.408	2.484	2.566 4.148	2.630 4.276	2.671 4.393	} $\times 10^{-5}$
Solvent = MeOH.							
Benzoic acid	77.03 95.16	3.769	4.066	4.393 3.795	4.790 4.128	5.156 4.430	} $\times 10^{-6}$
Salicylic acid	64.36 74.15	3.020	3.310 3.178	3.642 3.475	3.902 3.780	4.230 4.077	} $\times 10^{-6}$
<i>o</i> -Nitrobenzoic acid	81.91 113.00	4.456 3.908	4.820 4.210	5.196 4.594	5.570 4.922	5.940 5.256	} $\times 10^{-5}$
<i>m</i> -Nitrobenzoic acid	73.03 101.80	1.456 1.924	1.615 1.758	1.801 1.690	1.978 1.426	2.172 1.272	} $\times 10^{-5}$
<i>o</i> -Aminobenzoic acid	53.65 68.21		6.247	6.533	6.724 6.860	6.983 7.112	} $\times 10^{-5}$
Cinnamic acid	33.54 40.40	0.802 0.739	0.872 0.805	0.939 0.879	1.009 0.942	1.152 1.018	} $\times 10^{-5}$
Phthalic acid	27.81 44.40	4.133	4.677	5.270 5.045	5.947 5.630	6.540 6.306	} $\times 10^{-5}$

TABLE I ( *contd.* )

Solute.	Conc.	25°	30°	35°	40°	45°
Solvent=Propyl alcohol.						
Benzoic acid	32.53	1.859	2.034	2.189	2.383	2.554
	65.40		1.599	1.710	1.802	1.918
} $\times 10^{-7}$						
<i>m</i> -Nitrobenzoic acid	60.93	1.428	1.622	1.828	2.031	2.248
	94.74		1.497	1.724	1.946	2.154
} $\times 10^{-7}$						
Cinnamic acid	22.19	5.922	6.511	7.158	7.720	8.280
	33.15		6.410	7.158	7.759	8.461
} $\times 10^{-7}$						
Phthalic acid	7.25	2.697	3.092	3.467	3.874	4.273
	11.00	3.182	3.593	4.077	4.547	5.017
} $\times 10^{-6}$						
Succinic acid	4.92	6.610	7.381	8.155	8.876	9.726
	9.480	9.726	10.680	11.850	13.200	14.090
} $\times 10^{-6}$						
Solvent=Butyl alcohol.						
Salicylic acid	22.72	6.334	7.075	7.715	8.206	8.786
	33.25		7.947	8.565	9.281	9.852
} $\times 10^{-7}$						
Solvent= <i>n</i> -Butyl alcohol.						
<i>o</i> -Nitrobenzoic acid	20.77	7.755	8.253	9.156	9.592	9.970
	46.93	10.400	11.330	12.220	13.220	14.390
} $\times 10^{-7}$						
<i>o</i> -Aminobenzoic acid	18.10	2.981	3.294	3.407	3.608	3.923
	26.14			3.857	4.090	4.344
} $\times 10^{-7}$						
Cinnamic acid	8.32		2.063	2.293	2.557	2.761
	15.22			2.575	2.800	3.072
} $\times 10^{-6}$						
Phthalic acid	4.25	1.159	1.273	1.385	1.494	1.619
	10.60			1.828	2.091	2.324
} $\times 10^{-6}$						
Succinic acid	2.62		2.442	2.671	2.883	3.115
	5.61			4.337	4.655	5.010
} $\times 10^{-6}$						

NOTE: Specific conductivity has been determined at five different temperatures but due to brevity of space it is given at two different temperatures.

## DISCUSSION

From the results given in Table I specific conductivity has been plotted against temperature. The results obtained from the plot of  $\mu-t$  can be divided into two categories. In the first category, we have put the systems which give a straight line plot for  $\mu-t$ , e. g. acetone-*o*-aminobenzoic acid, acetone-salicylic acid, methyl alcohol-*m*-nitrobenzoic acid, propyl alcohol-succinic acid, etc. and therefore these solutions obey the Walden equation,

$$\mu t = \mu_o (1 + at) \quad \dots \quad (1)$$

within the temperature range studied here. It may be pointed out that no abrupt change occurs in the plot of  $\mu-t$  when the solution passes from the saturated to the supersaturated region.

The solutions in the second category, e. g. propyl alcohol-*m*-nitrobenzoic acid, propyl alcohol-benzoic acid, methyl alcohol-benzoic acid, acetone-phthalic acid, etc., do not obey Walden's equation and curvature is observed in the plot of  $\mu-t$  for these solutions. These solutions probably obey the equation of Kohlrausch

$$\mu t = \mu_0 (1 + \alpha t + \beta t^2) \quad \dots \quad (2)$$

*Relation between Conductivity and Viscosity.*—In the case of plot of  $\log \mu/1/T$  (this *Journal*, 1949, 26, 78) we obtained straight line plots for the solutions in acetone, propyl and butyl alcohols, but the plots for  $\log \mu/1/T$  for the solutions in methyl alcohol were generally not a straight line. Whereas in the case of plot of  $\mu-t$ , solutions in methyl alcohol generally give straight line plots but the solutions in acetone, propyl and butyl alcohols do not give a straight line plot. In the case of solutions in methyl alcohol the linearity for the plot of  $\mu-t$ , is more marked probably due to a higher value of dielectric constant of methyl alcohol than propyl and butyl alcohols where the dielectric constant is low, and so the conductivity is also low. Generally, when the conductivity is low, the plot of  $\mu-t$  is not a straight line, e. g. in the case of the solution of benzoic acid in methyl alcohol.

Although no exact relationship between the conductivity and structure of the acids can be obtained, as the concentrations studied for the different solutions are different, but a qualitative idea can be obtained from a consideration of the results given in Table I.

If we compare the results for the specific conductivity for the solutions of different solvents and the same solute, it is observed that the conductivity of solutions in methyl alcohol is more than that of the solutions in propyl and butyl alcohols. This is due to the fact that the dielectric constant of methyl alcohol is 31.2, that of propyl alcohol is 22.2 and butyl alcohol, 19.2. Conductivity of methyl alcohol solutions is about 100 times more than that of propyl alcohol solutions, but there is not much difference between the values of conductivity for the solutions of propyl and butyl alcohols e. g. conductivity of succinic acid in propyl alcohol is twice than that of butyl alcohol. As has been pointed out by Hunt and Briscoe (*loc. cit.*) this may be due to the fact that the separation of a methyl group from a hydroxyl group, i. e. OH by a CH<sub>2</sub> group does not alter the value of specific conductivity much, but the insertion of the second CH<sub>2</sub> group changes the conductivity values quite appreciably.

The conductivity of the solutions in acetone is equal to that of the solutions in propyl and butyl alcohols although the dielectric constant of acetone is 20.7 and is nearly equal to the dielectric constant of butyl and propyl alcohols, but the viscosity of acetone is very much less than these two alcohols. According to the above values of viscosity and dielectric constant, the conductivity of acetone solutions should have been higher than the solutions in butyl and propyl alcohols, but it is not so. No explanation is yet possible for these results.

It has been observed that the substitution of OH, NO<sub>2</sub> and NH<sub>2</sub> group in benzoic acid increases the conductivity of benzoic acid progressively. The effect of NH<sub>2</sub> group is more than NO<sub>2</sub> group, which is more than OH group for the solutions in methyl, propyl and butyl alcohols and acetone. Similar results have been obtained for the molecular conductivities of these acids in ethyl alcohol by Hunt and Briscoe (*loc. cit.*).

Conductivity of *o*-nitrobenzoic acid in methyl alcohol and acetone is more than that of *m*-nitrobenzoic acid solutions in these two solvents. Results have been explained by Briscoe and Hunt on the basis of the electronic theory of valence and current theories of molecular structure.

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CHEMICAL LABORATORIES,  
UNIVERSITY OF LUCKNOW,  
LUCKNOW.

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## A NOTE ON THE ISOLATION OF SAKURANIN, A GLUCOSIDE FROM THE BARK OF *PRUNUS PUDDUM* (N. O. ROSACEAE)

BY DUHKHAHARAN CHAKRAVARTY AND BISWANATH SEN

The stem bark of *Prunus Puddum* has been shown in this laboratory to contain a flavone, Puddumetin, which has been shown to be identical with Genkwanin (7-methoxy-5:4'-dihydroxyflavone; Chakravarti and Ghose, this *Journal*, 1944, 21, 171), a flavone, Sakuranetin (7-methoxy-5:4'-dihydroxyflavone; Chakravarti, Kundu and Ghosh, *ibid.*, 1948, 25, 329) and an isoflavone, which has been named Prunusetin (Chakravarti and Bhar, *ibid.*, 1945, 22, 301).

Though this work is being continued in this laboratory for more than five years, recently Narasimhachari and Seshadri (*Proc. Ind. Acad. Sci.*, 1949, 30, A, 271) have published a paper in this line and hence it is necessary to put on record our observations.

The note describes the isolation of another component from the bark of *Prunus Puddum*, the glucoside Sakuranin, which was isolated by Asahina, Shinoda and Inubuse

(*J. Pharm. Soc. Japan*, 1927, 550, 133 ; 1928, 553, 29) from the bark of *Prunus Pseudo Cerasus* and the most noteworthy observation is that the specimen of the bark from which the glucoside has been isolated contains only traces of the other components, e. g. Puddumetin, Sakuranetin and Prunusetin. Probably the chemical composition of the bark is dependent on the seasonal variation or it might be possible that the different components are present in different layers of the bark, as it has been observed that the glucoside occurs particularly in the immature bark of trees which are not very old.

A trace of another glucoside has also been isolated and it is being further investigated.

*Isolation of the Glucoside from the bark of Prunus Puddum.*—The powdered bark (2400 g., in 4 lots) was extracted with ether in a Soxhlet apparatus, and each lot was extracted with about one and a half litres of ether for 16 to 18 hours.

The ethereal extract, which was orange-yellow in colour, was filtered, and the ether was completely removed by distillation. The residue was obtained as a reddish brown gelatinous mass. The gelatinous mass was repeatedly (3-4 times) treated with about 50 c. c. of cold benzene, with which it was thoroughly mixed, and the supernatant clear benzene layer decanted off. The residue was then dried in vacuum and the dried mass dissolved in the minimum amount of boiling absolute alcohol, after which the solution was allowed to stand for about a week, but no crystals separated. The alcohol was completely removed and the pasty mass was refluxed with small amounts of dry benzene for several times (4-5 times). The pasty residue was then dissolved in the minimum amount of boiling absolute alcohol and the solution on standing for several days deposited a solid, which could not, however, be collected by filtration on account of the presence of much slimy matter in the mother-liquor.

The supernatant alcoholic mother-liquor was decanted off very carefully and the solid was washed with anhydrous benzene and the wash benzene was decanted into mother-liquor, when a pasty mass was precipitated. By repeated treatment with absolute alcohol and washing with benzene, a solid was obtained which crystallised from absolute alcohol as needles, m. p. 213-14°.

The yield of the glucoside is roughly 0.05% of the weight of the dried bark. It is soluble in water, ethyl alcohol, sparingly soluble in ether and insoluble in benzene. (Found in sample dried in vacuum at 130-140° for 8 hours : C, 58.88 ; H, 5.38. Calc. for  $C_{22}H_{24}O_{10}$  : C, 58.86 ; H, 5.36 per cent).

*Hydrolysis of the Glucoside : Isolation of Sakuranetin and Glucose.*—The glucoside (1 g.) was refluxed with sulphuric acid (5%, 40 c. c.) for  $\frac{1}{2}$  hour. The solution was filtered and the residue crystallised from alcohol (charcoal) and from benzene, m. p. 150-51° (mixed melting point with the sample of sakuranetin isolated from the bark of *Prunus Puddum* in this laboratory). (Found : C, 66.8 ; H, 4.8 ; OMe, 10.90. Calc. for  $C_{16}H_{14}O_6$  : C, 67.0, H, 4.9 ; OMe, 10.8 per cent).

Sakuranetin monomethyl ether (m.p. 116-117°) and sakuranetin oxime (m.p. 201-203°), prepared from this sample were identical in all respects with the derivatives of an authentic sample of sakuranetin.

The filtrate after hydrolysis gave on treatment with phenylhydrazine acetate, as usual, glucosazone (m.p. 205-206°, mixed m.p. with an authentic sample of glucosazone).

CHEMICAL LABORATORY,  
UNIVERSITY COLLEGE OF SCIENCE,  
CALCUTTA.

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## A NOTE ON PERIODATES OF CADMIUM

BY SURJIT SINGH AND APPAR SINGH

The following periodates of cadmium are reported in literature :

1. Secondary cadmium mesoperiodate,  $\text{CdHIO}_5$ .
2. Cadmium metaperiodate,  $\text{Cd}(\text{IO}_4)_2$ .
3. Trihydrated cadmium diparaperiodate,  $\text{Cd}_4 \text{I}_2 \text{O}_{11}, 3\text{H}_2\text{O}$ .
4. Pantahydrated cadmium mesoperiodate,  $\text{Cd}_3(\text{IO}_5)_2, 5\text{H}_2\text{O}$ .
5. Ennehydrated cadmium dimesoperiodate,  $\text{Cd}_2 \text{I}_2 \text{O}_9, 9\text{H}_2\text{O}$ .

Out of the five periodates of cadmium only two were found to be formed, viz., secondary cadmium mesoperiodate,  $\text{CdHIO}_5$ , and hexahydrated cadmium mesoperiodate,  $\text{Cd}_3(\text{IO}_5)_2, 6\text{H}_2\text{O}$ , as described below.

Secondary cadmium mesoperiodate,  $\text{CdHIO}_5$ , was prepared by adding an excess of a hot solution of periodic acid to a warm suspension of cadmium carbonate in water. The excess of the acid was ensured by litmus paper. The mixture was stirred and kept hot till there was no effervescence. A fine gelatinous precipitate was formed which turned granular on standing. It was filtered, washed with water till free from the acid and then dried at 60° in a hot air-oven. It was analysed as follows.

The cadmium content of the periodate was determined by the pyridine method (Vogel, "Quantitative Inorganic Analysis," 1946, p. 510).

The percentage of iodine in the periodate was found by Kimmins' method as modified by Bahl and Partington (*J. Chem. Soc.*, 1934, 1088).

Available oxygen was estimated by the method adopted by Bahl and Partington (*loc. cit.*).

TABLE I

No.	%Cd.	%I <sub>2</sub> .	%Available O <sub>2</sub>
1.	35.10	40.07	18.00
2.	35.12	40.00	17.90
3.	35.20	40.00	17.90

The above results agree with the formula of the secondary cadmium mesoperiodate, CdHIO<sub>5</sub>. The calculated values being, Cd, 35.0%; I<sub>2</sub>, 39.7% and available oxygen according to the decomposition,  $2\text{CdHIO}_5 \rightarrow 2\text{CdO} + \text{I}_2 + 3\text{O}_2 + \text{H}_2\text{O}$ , is 17.60%.

Hexahydrated cadmium mesoperiodate, Cd<sub>3</sub>(IO<sub>5</sub>)<sub>2</sub> · 6H<sub>2</sub>O was prepared by the addition of a hot solution of secondary sodium paraperiodate in dilute nitric acid or a hot solution of potassium metaperiodate in water to an excess of cadmium sulphate with constant stirring. The mixture was boiled for some time to ensure the completion of the reaction. The insoluble periodate formed was filtered, washed free of the soluble salts with water, and dried at 60° in a hot air-oven. It was analysed as above.

TABLE II

A				B			
No.	%Cd.	%I <sub>2</sub> .	%Available O <sub>2</sub>	No.	%Cd.	%I <sub>2</sub> .	%Available O <sub>2</sub>
1.	39.20	29.60	12.90	1.	39.20	29.80	12.95
2.	39.48	29.40	12.09	2.	39.32	29.40	13.12
3.	39.70	29.18	13.0	3.	39.18	29.12	13.10

Calc. for Cd<sub>3</sub>(IO<sub>5</sub>)<sub>2</sub> · 6H<sub>2</sub>O : Cd, 39.16; I<sub>2</sub>, 29.14; available oxygen, 13.05%.

The authors wish to offer their sincere thanks to S. Sachdev Singh, Head of the Chemistry Dept., Govt. College, Ludhiana for affording all the facilities for doing the above work.

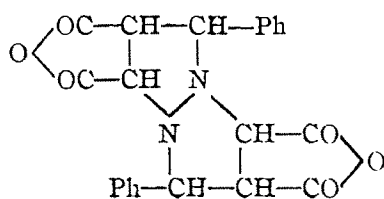
## REACTION OF *cyclo*HEXANONE-AZINE WITH DIENOPHILS

By D. B. DUTT AND P. C. GUHA

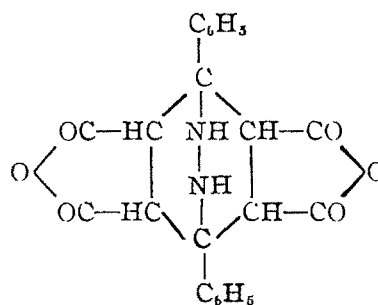
Crisscross addition of *cyclo*hexanoneazine and maleic anhydride has been studied with the formation of an adduct.

Azines though like typical dienes contain a conjugated system of double bonds, fail to undergo Diels-Alder reaction. In this connection reaction of benzalazine with maleic anhydride has been thoroughly studied. Snyder and co workers reported the formation of benzalmalein hydrazine (*J Amer. Chem. Soc.*, 1934, **60**, 2025). Wagner-Jauregg found that two molecules of maleic anhydride reacted with one molecule of benzalazine to give small yields of a product, to which he assigned the structure (I) (*Ber.*, 1930, **63**, 3224). Van Alphen pointed out the possibility of structure (II) and favoured (I) on the following grounds (*Rec. trav. chim.*, 1942, **61**, 892).

1. The compound cannot be benzoylated or acetylated and therefore contains no NH group.
2. The substance is stable towards reducing agents, while it might be expected that the hydrazine linkage would be opened in (II).
3. An intermediary product with one molecule of maleic anhydride cannot be isolated.



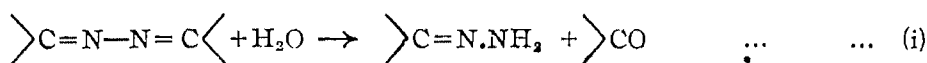
(I)



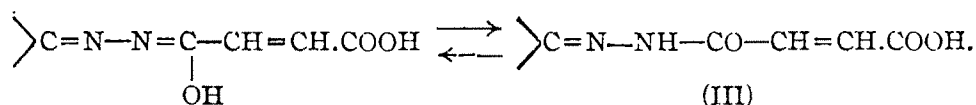
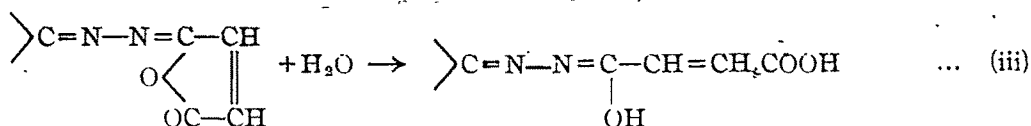
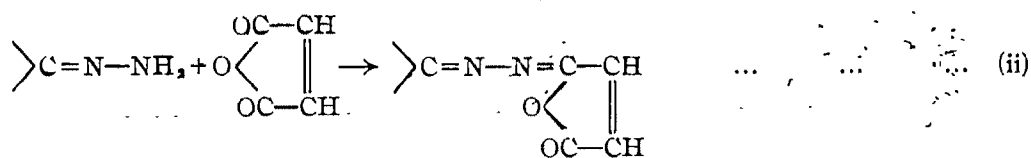
(II)

He subsequently showed that the crisscross addition of maleic anhydride to the azine system was a general reaction of aromatic aldazines, while this 1:3 addition failed with acetoneazine, acetophenoneazine and acetaldehydeazine (*ibid.*, 1942, **61**, 895).

Recent investigations of Gartaro Coroma show that the nature of solvent plays a dominant role in the action of maleic anhydride with azines. In presence of the slightest trace of water maleic hydrazides (III) are formed, the amount of product increasing with the moisture content, up to a certain maximum. The course of reaction is reported to be as follows.

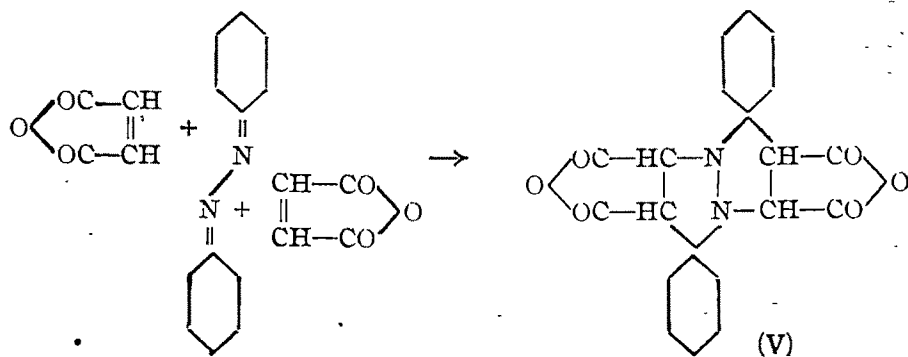
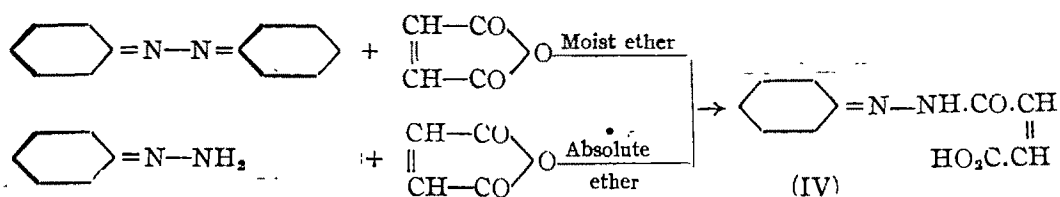






Snyder *et al.* had obtained benzalmaleinhydrazine by reacting benzalazine and maleic anhydride in moist ether and proposed similar course for the reaction (*loc.cit.*).

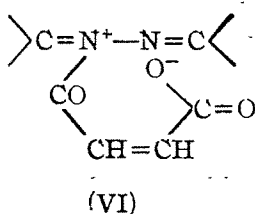
During our experiments with hydroaromatic ketazines, contrary to expectations, we observed that these azines very readily reacted with cyanic and thiocyanic acids to give crisscross adducts (*Cur. Sci.*, 1949, 18, 297). Our success with the above reagents prompted us to study the reaction further with maleic anhydride and other dienophils. We found that *cyclohexanoneazine* reacted with maleic anhydride to give a variety of products, depending upon the conditions of reaction. In moist ether the reaction proceeds readily in cold, one molecule of ketazine reacting with maleic anhydride to give *cyclohexylidene-maleinhydrazine* (IV). The same product is obtained, in nearly quantitative yield, by reacting *cyclohexylidene-hydrazone* with maleic anhydride in absolute ether, but not so readily by reacting the ketazine with maleic anhydride in absolute ether or anhydrous benzene.



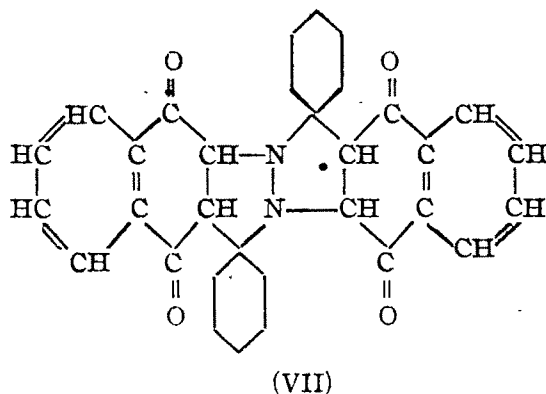
By refluxing one molecule of *cyclohexanoneazine* with two molecules of maleic anhydride in anhydrous benzene, toluene or xylene a different course of reaction is followed and besides a small amount of resin, the expected crisscross adduct 4:8-dicyclohexylidene-1:5-diazo-bicyclo- (0:1:5)-octane-2:3:6:7-tetracarboxic anhydride (V) is formed.

In moist ether, besides (IV), a small quantity of the 1:3:2:4 adduct (V) is also formed.

The resinous compound formed is insoluble in ether and benzene, but soluble in alcohol, from which it is obtained back as a viscous resinous mass, after evaporation. The properties of the resinous compound agree well with the salt-like addition product (VI), described by Van Alphen for Schiff's bases and azines with one molecule of maleic anhydride (*loc. cit.*). The resinous compound immediately decolorises Baeyer's reagent and bromine water and is split up by dilute sulphuric acid, *cyclohexanone* being one of the products. The quantity of resin increases if maleic anhydride and the azine are taken in molar proportions. In all our experiments small quantities of this resin were formed.

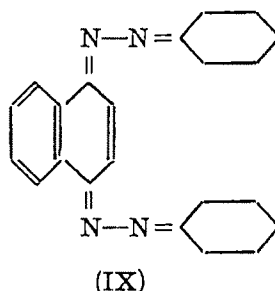
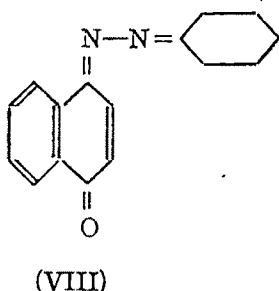


Our observation of crisscross addition of maleic anhydride and *cyclohexanoneazine* are interesting as, so far we are aware, this is the first observed case of such addition with a ketazine. Van Alphen remarked that with the exception of the crisscross addition of benzalazine it was found that none of the groups:  $C=N-N=C$ ,  $N=C-C=N$  or  $C=C-C=N$  are capable of adding maleic anhydride just like butadienes (*loc. cit.*, p. 895).



Crisscross addition of  $\alpha$ -naphthoquinone was next tried with the object of preparing polycyclic compounds like (VII). With benzalazine no reaction takes place in boiling anhydrous xylene. When fused together at  $150^\circ$  for 15 minutes, two compounds are formed, one greenish solid (decomp.  $275^\circ$ - $280^\circ$ ) crystallising from glacial acetic acid, and

a tough brown resin, melting indistinctly at about  $65^{\circ}$ . With *cyclohexanoneazine* a small amount of a brown-black solid is formed on long boiling in xylene and exposure to atmosphere. The reaction is presumably preceded by the hydrolysis of the ketazine to hydrazone and subsequent reaction of the hydrazone with the quinone to give ketazine (VIII) or (IX).



The view is supported by the reaction of *cyclohexylidene-hydrazone* with  $\alpha$ -naphthoquinone in anhydrous xylene to give the same product (m.p.  $305-307^{\circ}$ ). Quinones are known readily to react with hydrazones to give mixed ketazines (cf. Gerhardt, *Monatsch*, 1921, 42, 63). The product (VII) could not be formed. Hence, we conclude that *cyclohexanoneazine* reacts readily with maleic anhydride to give the crisscross adduct, while no such reaction takes place with  $\alpha$ -naphthoquinone.

#### E X P E R I M E N T A L

*cycloHexanoneazine*.—To *cyclohexanone* (9.8 g.) was added 85% hydrazine hydrate (6 c.c.) with shaking. Heat was developed and the mixture became cloudy. The mixture was heated on a water-bath ( $90-95^{\circ}$ ) for one hour and kept overnight. On saturating with potassium hydroxide an oily layer separated. Fractional distillation gave *cyclohexanonehydrazone* (1.5 c.c.) at  $90-92^{\circ}/11$  mm. and pure ketazine at  $120^{\circ}-122^{\circ}/3-4$  mm. Yield of the ketazine was 7.5 g., m.p.  $33^{\circ}$ .

*cycloHexylidene-maleinhydrazine*: (a) *From cycloHexanonehydrazone*.—Maleic anhydride (1 g.) was dissolved in 15 c.c. of absolute ether and *cyclohexanone hydrazone* (1.1 g.) was added. Immediately the solution warmed up and a yellow solid started crystallising and the mixture was kept for 3 hours at  $25^{\circ}$ . The separated crystals melted at  $172^{\circ}$  and the melting point was raised to  $178^{\circ}$  by washing with hot alcohol. The compound dissolves sparingly in absolute alcohol and crystals from alcohol shrink at  $178^{\circ}$  melting sharply at  $180^{\circ}$ , yield 1.4 g. (Found: N, 12.9.  $C_{10}H_{14}O_3N_2$  requires N, 13.3 per cent).

The compound is insoluble in most of the organic solvents when cold. In warm dioxane the solution immediately decolorises Baeyer's reagent. In dilute alkali the compound readily dissolves, showing acidic properties. It is insoluble in cold water and gets hydrolysed by boiling water, maleic acid being liberated. The substance (0.1678 g.) on refluxing with 25 c.c. of distilled water for 2 hours requires 20.1 c.c. of 0.818 N sodium hydroxide solution.

(b) *From cycloHexanoneazine*.—To maleic anhydride (2 g.), dissolved in 25 c.c. of moist ether *cyclohexanoneazine* (2 g.) was added. The mixture assumed a pale yellow colour and became turbid within fifteen minutes; it was kept in a refrigerator for 16 hours. A pale yellow solid settled down. The ether layer was separated and the solid refluxed in absolute alcohol for half an hour. Major part was left undissolved as a yellow crystalline solid, m.p. 178–80°, yield 1.1 g. On washing with hot alcohol melting point became constant at 180° and there was no depression when mixed with *cyclohexylidene-maleinhydrazine* as prepared in (a).

Ether layer on evaporation left a viscous liquid which when triturated with hot alcohol gave a solid crystalline product (0.19 g.), m.p. 288°. Mixed melting point shows it to be the crisscross adduct (V). The viscous liquid also contains *cyclohexanone* (semicarbazone, m.p. 166°) and maleic acid (m.p. 129; showing no depression with a known sample).

4:8-Dicyclohexylidene-1:5-diazobicyclo- (0:1:5)-octane-2:3:6:7-tetracarboxylic Anhydride (V).—*cycloHexanoneazine* (2 g.), maleic anhydride (3 g.) and anhydrous sodium-dried benzene (25 c.c.) were refluxed on a water-bath. The solution gradually changed from pale yellow to orange-red and then a pinkish resin started separating. After a period of four hours quite a good amount of the resinous mass separated and benzene stopped refluxing. Absolute alcohol (25 c.c.) was added and the mixture further refluxed for 15 minutes. On filtering hot a greyish white solid was left, m.p. 285–87°, yield 2.6 g. On repeatedly washing with boiling alcohol the melting point rose to 290–91°. (Found: N, 6.9.  $C_{20}H_{24}O_8N_2$  requires N, 7.22 per cent).

On evaporating the filtrate a yellow-brown resinous mass was left, insoluble in ether and benzene, but soluble in alcohol from which it was obtained in the same condition on evaporating off the solvent. Alcoholic solution decolorises Baeyer's reagent. It is partly soluble in hot water and the aqueous extract decolorises bromine water immediately and shows acidic reactions. The resin is vigorously decomposed by dilute sulphuric acid. All these reactions support structure (VI) (cf. Van Alphen, *loc. cit.*).

By refluxing *cyclohexanoneazine* (1 g.) and maleic anhydride (0.5 g.) in anhydrous benzene (10 c.c.) the main product was the resin, very small amount of the solid crisscross adduct (V) separating.

## ADSORPTION OF ACIDS, BASES AND ALKALOIDS BY SYNTHETIC ION-EXCHANGE RESINS

BY SUDHAMOY MUKHERJEE, MANIK LAL SEN GUPTA AND  
RABINDRA NATH BHATTACHARYYA

The adsorption of acids and alkalis on synthetic resins follows the Freundlich adsorption isotherm. The results indicate surface adsorption rather than chemical interaction between the functional groups on the surface of the resins and the acid or alkali in solution.

The order of the total acidities of the cationic resins, as determined by potentiometric titrations with alkali, may not agree with that of the adsorptive powers as found from the adsorption isotherms. The study of both adsorption isotherms and titration curves would afford a more complete picture of the adsorption characteristics.

The anionic resins appear to exhibit true anion-exchange rather than molecular adsorption of acids.

The order of adsorption of alkaloids, in a number of cationic resins, does not agree with that for alkali as obtained from titration curves, and further, this order varies with different alkaloids.

Adams and Holmes (*J. Soc. Chem. Ind.*, 1935, 54, 11) first drew attention to the adsorbing powers of resins from polyhydric phenols and formaldehyde for various cations. Bhatnagar and co-workers (this *Journal*, 1936, 13, 679 ; 1939, 16, 249, 262, 361) concluded that adsorption from solutions by these resins followed the ordinary laws of adsorption and hence must be considered a surface phenomenon.

Myers ("Advances in Colloid Science", Vol. I, Interscience Publishers, Inc., New York, 1942, p. 333) considered that the exchange phenomena on synthetic resins should be regarded as metathetical chemical reactions between the electrolytes in solution and the active groups on the surface. This primary process is, however, so masked by diffusion and reaction velocity factors, that the practical equilibrium values simulate adsorption phenomena.

Equations of exchange equilibria for cation-exchange resins were formulated by Griessbach ("Über die Herstellung und Anwendung neuerer Austausch adsorbierenten, insbesondere auf Hartzbasis", Verlag Chemie, Berlin, 1939) on the basis of the Freundlich adsorption isotherm and by Boyd, Schubert and Adamson (*J. Amer. Chem. Soc.*, 1947, 69, 2818) on the basis of the Langmuir isotherm as well as of the law of mass action. There now appears to be a general agreement regarding the fundamental nature of cation-exchange on synthetic resins. But since the observed characteristics vary from one resin to another, depending upon the nature of the acidic groups and the texture (which determines available surface and accessibility of the active groups), the necessity is felt for further data on the characteristics of various types of synthetic resins with a view to judging their suitability for application in different fields.

With anion-exchange resins, however, the nature of the interactions is not so clear. Until recently, the view was prevalent that these amine type resins adsorb acids molecularly instead of exchanging anions (Schwartz, Edwards and Boudreaux, *Ind. Eng. Chem.*, 1940, 32, 1462 ; Griessbach, *loc. cit.*) On the other hand, the work of Jenny

(*J. Colloid Sci.*, 1946, **1**, 33), Sussman (*Ind. Eng. Chem.*, 1945, **37**, 618) and of Kunin and Myers (*J. Amer. Chem. Soc.*, 1947, **69**, 2874) indicate that these are true anion exchangers. Further evidence seems to be necessary for the clarification of the mechanism of adsorption by anion-exchange resins.

Most of the industrial applications on ion-exchange resins, till now, have been in the field of water de-ionisation, and the methods of characterisation and evaluation of the resins, developed so far, are mostly concerned with the requirements of water-treatment operations. There is, however, promise of the large-scale employment of synthetic ion-exchange resins for other purposes as well, e.g., for the isolation of alkaloids (cf. Applezweig and Ronzone, *Ind. Eng. Chem.*, 1946, **38**, 576; Mukherjee, *J. Proc. Inst. Chem. (India)*, 1947, **19**, 61). Preliminary observations on the adsorption and elution of quinine on ion-exchange columns have been made in this laboratory (Mukherjee and Sen Gupta, *ibid.*, 1949, **21**, 83), but irregularities have often been noticed, which have been ascribed to the kinetics of the ion-exchange process.

In the present work, studies have been made on the fundamental adsorptive properties of a number of synthetic cation- and anion-exchange resins, available in the market, as also on the adsorption of alkaloids by cationic resins, both under static and dynamic (column) conditions.

#### EXPERIMENTAL

*Synthetic Resins.*—Three cationic resins—Zeokarb\*, amberlite IR-100\*\* and Ionac C-284†, and two anionic resins—Deacidite\* and Ionac A-293† were used for the experiments.

*Preparation of Standard Forms of Resins.*—For preparing the *hydrogen form* the cationic resin was kept in contact with standard sulphuric acid, with frequent shaking. After 24 hours, the acid was decanted off and its strength determined and fresh standard acid added to the resin. This was repeated until the acid suffered no loss of strength after 24 hours' contact with the resin. The actual period of contact required was in most cases 72 hours. The resin was washed with water and kept under water with intermittent shaking. After 24 hours the water was filtered off and estimated for acid content and the resin suspended in fresh water. This was continued until the wash water did not show titratable acidity after 24 hours' contact. The resin was dried to a constant weight at 40°.

For determining the residual acid in the resin, 1 g. of the latter was kept in contact with 50 c.c. of water for one week with intermittent shaking. The acidity of the water was estimated at the end of this period.

The *alkali forms* of the anionic resins were prepared in a similar manner, replacing the standard acid with standard caustic soda solution.

"Acid forms" of the anionic resins and "alkali forms" of the cationic resins were prepared in the following manner. The resin was kept in contact with 0.1N sulphuric acid or caustic soda solution, with periodical replacement, till "saturation" was reached.

\*From the Permutit Company, U. S. A.

\*\*From the American Cyanamid Company, U. S. A.

†From the Resinous Products & Chemical Company, U. S. A.

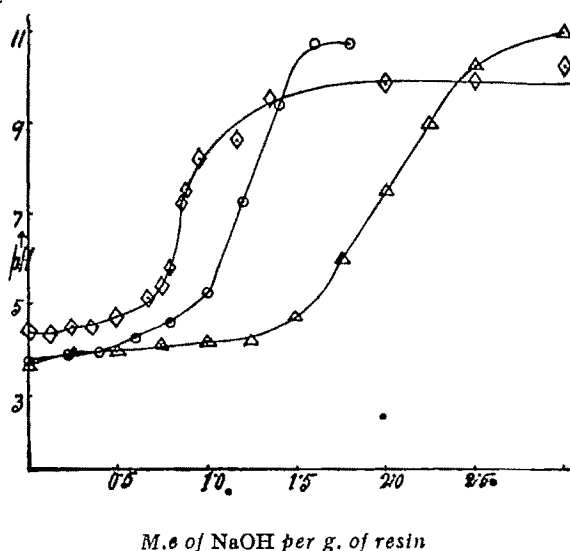
It was filtered and washed on the filter with alcohol in order to remove free acid or alkali adhering to the resin and dried to a constant weight at 40°.

*Adsorption Measurements.*—The resin (1 g.) was suspended in 50 c. c. of the appropriate solution of the electrolyte, kept for 24 hours with intermittent shaking, and the solution was then analysed.

*Potentiometric Titrations.*—The acid forms of the cationic resins were titrated potentiometrically with caustic soda and the alkali forms of the anionic resins similarly titrated with sulphuric acid. The standard forms, prepared using 1*N* solutions of acid or alkali, were used for this purpose. Varying amounts of 0.1*N* sulphuric acid or caustic soda were taken in a series of reagent bottles, water was added to bring the volume to 10 c. c. in every case, and 0.2 g. of the resin was added to each bottle. The mixture was shaken intermittently and allowed to stand for 24 hours after which the  $p_H$  of the supernatant liquid was determined with a  $p_H$  meter. (It was found by a preliminary experiment that increasing the period beyond 24 hours did not produce any further change of  $p_H$ ). The results have been plotted graphically in Figs. 1 and 2.

FIG 1

*Potentiometric titration curves of acid forms of cationic resins with NaOH.*



The curve indicated by rectangle refers to H-Zeocrab-215, that by triangle, H-Ionac-C-284 and the one by circle, H-Amberlite IR-100.

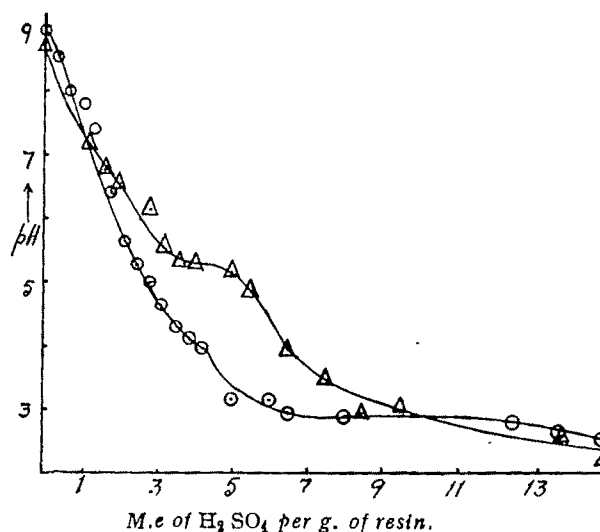
#### Standard Forms of Synthetic Resins

For purposes of characterisation and comparison of exchange capacities of different resins, these should be reduced to standard conditions (*i. e.* to hydrogen or hydroxyl forms). But reference to the literature does not show any uniformity of procedure in this respect. Various concentrations of acid or alkali have been recommended for

this purpose, e.g., 1 or 2% (Myers, Eastes and Myers, *Ind. Eng. Chem.*, 1941, 88, 697), 2% (Myers and Eastes, *ibid.*, 1941, 88, 1203), 1 N (Kunin and Myers, *loc. cit.*) and 5N (Boyd, Schubert and Adamson, *loc. cit.*).

FIG. 2

Potentiometric titration curves of alkali forms of anionic resins with  $H_2SO_4$ .



The upper curve refers to Na-Deacidite and the lower one to Na-Ionac A-293.

In view of the above, a study was made of the effect of concentration of acid or alkali on the properties of the resultant acid or alkali forms of the resins. The acid forms of the cationic resins were prepared with 0.1N and 1.0N sulphuric acid and those of the anionic resins were prepared using 1.0N caustic soda. For one cationic resin, Amberlite IR-100, the acid forms were prepared using 3N acid also.

The alkali or acid consumptions from 0.1N solutions by the acidic or alkaline resins, respectively, were determined and the results are given in Table I. The adsorption has in all cases been expressed in terms of normal acid or alkali consumed per g. of the resin.

TABLE I

Synthetic resins.	1.0N- $H_2SO_4$ or NaOH consumed by 1 g of resin treated with $H_2SO_4$ or NaOH		
	0.1N.	1.0N.	3.0N.
Amberlite IR-100 ( $H_2SO_4$ -treated)	2.86 c.c.	2.75	2.88
Zeokarb 215 ( $H_2SO_4$ -treated)	3.70	2.93	—
Ionac C-284 ( $H_2SO_4$ -treated)	3.52	3.50	—
Ionac A-293 (NaOH-treated)	4.10	4.18	—
Deacidite (NaOH-treated)	5.00	5.00	—



The above results show that the standard forms are independent of the concentration of the acid or alkali used for their preparation. The discrepancy observed with Zeokarb should probably be attributed to incomplete washing of the acid resin prepared with 0.1N acid. For this resin, the latter form was not used in any subsequent studies.

The presence of free and diffusible acid or alkali in the standard forms of resins was investigated by keeping the resins in contact with water for seven days (Table XI). The results show that acid forms of cationic resins or the alkali forms of anionic resins contain negligible amount of free acid or alkali, but the opposite numbers contain an appreciable amount of free acid or alkali. This has been referred to later again.

#### *The "Suspension effect" in Synthetic Resins*

Wiegner and Pallman (Sub Kommission der Internationalen, Boden. Gessel., 1929, p. 92) observed that in certain aqueous suspensions the supernatant liquid had a different  $p_H$  from that of the suspension. Mukherjee, Mitra and Mukherjee (*Trans. Nat. Inst. Sci.*, 1937, 1, 227) observed the same phenomenon in colloidal suspensions of acidic substances, viz., silicic acid, palmitic acid and hydrogen clays, and attributed this to the osmotic activity of the mobile hydrogen ions in the liquid side of the electrical double layer on the surface of the particles. The acid forms of the cationic resins should also come under this category, and so determinations were made of the  $p_H$  of the supernatant liquid and of the moist resin residue after removing most of the free water by decantation, using a glass electrode. For the latter determinations, care was taken to pile up the resin magma around the electrode to ensure efficient contact with the electrode surface and to maintain electrolytic contact. Equilibrium was attained slowly and the final readings were taken when constant values of  $p_H$  were obtained. The determinations were made on suspensions at an advanced stage of washing, and the supernatant liquids were in contact with the resins for 48 hours, with frequent shaking, before the measurements were taken in order to ensure the establishment of equilibrium. The results are given in Table II.

TABLE II

#### *Suspension effect in synthetic resins.*

Synthetic resins and treatment with acid, *	Supernatant liquid.	$p_H$ of	Resin magma.
Amberlite IR-100 treated with 0.1N-H <sub>2</sub> SO <sub>4</sub>	4.86		2.00
„ „ 1.0 „	3.48*		2.04
„ „ 3.0 „	4.38		2.00
Zeokarb „ 1.0 „	4.56		2.24
Ionac C284 „ 1.0 „	4.00		2.08

\*A large ratio of resin: water was used in this case.

The results show a significant difference between the  $p_H$  of the supernatant liquid and the resin magma, and point to the existence of a suspension effect in these cases also.

*Adsorption of Acids, Alkali and Neutral Salts by Standard Forms of Resins*

The acid and alkali forms of resins, used for these experiments, were prepared using 0.1N sulphuric acid or caustic soda, excepting Zeokarb, for which 1.0N concentration of acid was used. The results are shown in Table III to XI.

TABLE III

*Adsorption of caustic soda by acid forms of cationic resins.*

Zeokarb 215			H-Amberlite IR-100		H-Ionac C-184	
Initial conc. of NaOH.	Equilib. conc. of NaOH.	Adsorption of NaOH. (c.c. of N-NaOH)	Equilib. conc. of NaOH.	Adsorption of NaOH. (c.c. of N-NaOH).	Equilib. conc. of NaOH.	Adsorption of NaOH. (c.c. of N-NaOH).
1.00N	0.8999N	5.0	0.9080N	4.60	0.9020N	4.90
0.50	0.4040	4.8	0.4120	4.40	0.4104	4.84
0.333	0.2440	4.46	0.2512	4.10	—	—
0.25	—	—	—	—	0.1660	4.20
0.20	0.1194	4.03	0.1296	3.52	0.1190	4.05
0.167	—	—	—	—	0.0860	4.03
0.143	0.0709	3.59	0.0783	3.22	—	—
0.125	0.0549	3.50	0.0629	3.10	0.0479	3.85
0.100	0.0374	3.13	0.0428	2.86	0.0296	3.52
0.067	0.0167	2.48	0.0204	2.31	0.0070	2.98

TABLE IV

*Adsorption of sulphuric acid by acid form of Zeokarb.*

Initial conc. of H <sub>2</sub> SO <sub>4</sub> .	Equilib. conc. of H <sub>2</sub> SO <sub>4</sub> .	Adsorption of H <sub>2</sub> SO <sub>4</sub> (c.c. of N-H <sub>2</sub> SO <sub>4</sub> ).
1.06N	1.051N	0.16
0.53	0.517	0.12
0.21	0.203	0.176
0.08	0.074	0.12
0.06	0.054	0.12
0.04	0.036	0.08

TABLE V

*Adsorption of sulphuric acid by alkali forms of anionic resins.*

Na-Deacidite			Na-Ionac A-293	
Initial conc. of H <sub>2</sub> SO <sub>4</sub> .	Equilib. conc. of H <sub>2</sub> SO <sub>4</sub> .	Adsorption of H <sub>2</sub> SO <sub>4</sub> (c.c. of N-H <sub>2</sub> SO <sub>4</sub> ).	Equilib. conc. of H <sub>2</sub> SO <sub>4</sub> .	Adsorption of H <sub>2</sub> SO <sub>4</sub> (c.c. of N-H <sub>2</sub> SO <sub>4</sub> ).
0.50N	0.3159N	9.53	0.3870N	5.65
0.20	0.0349	8.25	0.0995	5.02
0.143	0.0038	6.95	0.0540	4.44
0.100	0.0000	5.00	0.0180	4.10

TABLE VI

*Adsorption of hydrochloric acid by alkali forms of anionic resins.*

Na-Deacidite			Na-Ionac A-293	
Initial conc. of HCl.	Equilib. conc. of HCl.	Adsorption of HCl (c.c. of N-HCl).	Equilib. conc. of HCl.	Adsorption of HCl. (c.c. of N-HCl).
0.50 N	0.3420N	7.90	0.4151N	4.25
0.20	0.0634	6.82	0.1201	4.00
0.143	0.0178	6.25	0.0700	3.64
0.100	0.0150	4.25	0.0320	3.40

TABLE VII

*Adsorption of sulphuric acid by alkali forms of cationic resins.*

Na-Zeokarb			Na-Amberlite IR-100		Na-Ionac C-284	
Initial conc. of H <sub>2</sub> SO <sub>4</sub> .	Equilib. conc. of H <sub>2</sub> SO <sub>4</sub> .	Adsorption of H <sub>2</sub> SO <sub>4</sub> . (c.c. of N-H <sub>2</sub> SO <sub>4</sub> )	Equilib. conc. of H <sub>2</sub> SO <sub>4</sub>	Adsorption of H <sub>2</sub> SO <sub>4</sub> . (c.c. of N-H <sub>2</sub> SO <sub>4</sub> ).	Equilib. conc. of H <sub>2</sub> SO <sub>4</sub> .	Adsorption of H <sub>2</sub> SO <sub>4</sub> . (c.c. of N-H <sub>2</sub> SO <sub>4</sub> ).
1.00N	0.9038N	4.80	0.9428N	2.86	0.9301N	3.40
0.50	0.4209	3.95	0.4468	2.66	0.4370	3.15
0.333	0.2590	3.71	0.2811	2.60	—	—
0.25	—	—	—	—	0.1930	2.85
0.20	0.1380	3.10	0.1508	2.46	0.1570	2.75
0.167	...	—	—	—	0.1120	2.73
0.143	0.0839	2.94	0.0946	2.40	—	—
0.125	0.0680	2.85	0.0783	2.32	0.0739	2.55
0.100	0.0439	2.80	0.0563	2.18	0.0520	2.40
0.0667	0.0152	2.57	0.0264	2.01	0.0216	2.25

TABLE VIII

*Adsorption of caustic soda by acid forms of anionic resins.*

H-Deacidite			H-Ionac A-293	
Initial conc. of NaOH.	Equilib. conc. of NaOH.	Adsorption of NaOH. (c.c. of N-NaOH).	Equilib. conc. of NaOH.	Adsorption of NaOH. (c.c. of N-NaOH).
0.50N	0.3819N	5.00	0.4185N	4.07
0.25	0.1395	5.52	0.1726	3.87
0.167	0.0600	5.30	0.0920	3.73
0.125	0.0180	5.35	0.0540	3.55
0.100	0.0043	4.78	0.0335	3.32

TABLE IX

*Interaction of salts with acid forms of cationic resins.*

Conc. of salt		Acid liberated in solution in terms of c. c. of N-HCl.		
KCl.	BaCl <sub>2</sub> .	H-Zeokarb.	H-Amberlite IR-100.	H-Ionac C-284
0.1N	—	1.325	0.825	—
0.2	—	1.50	0.85	1.575
1.0	—	1.625	0.925	—
—	0.1N	1.625	0.95	—
—	0.2	1.65	1.025	1.725
—	1.0	1.675	1.025	—

TABLE X

*Interaction of salts with alkali forms of anionic resins.*

		Alkali liberated in solution (c.c. of N-KOH).	
Salt used.	Conc. of salt.	Na-Deacidite.	Na-Ionac A-293.
KCl	0.2N	0.5	0.15
K <sub>2</sub> SO <sub>4</sub>	0.2	0.8	0.10
K <sub>2</sub> HPO <sub>4</sub>	0.2	0.8	0.40

TABLE XI

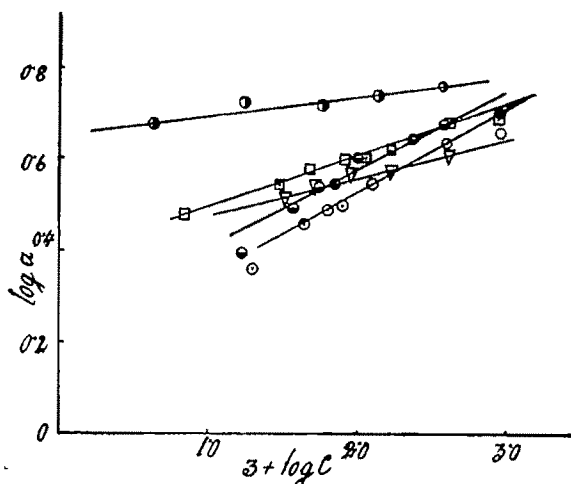
*Free acid or alkali in standard forms of resins.*

(After 7 days' contact with water)

		Liberation of free acid or alkali	
Resin used.	Standard form.	N-H <sub>2</sub> SO <sub>4</sub> .	N-NaOH.
Zeokarb	Acid	0.02 c.c.	—
"	Alkali	—	0.63 c.c.
Amberlite IR-100	Acid	0.025	—
"	Alkali	—	0.46
Ionac C-284	Acid	0.048	—
"	Alkali	—	0.08
Deacidite	Acid	0.25	—
"	Alkali	—	0.05
Ionac A-293	Acid	0.62	—
"	Alkali	—	0.02

*Adsorption of Alkali.*—Figures 3 and 4 contain curves obtained by plotting the logarithms of the amounts adsorbed against the logarithms of the equilibrium concentrations of the adsorbate in solution. It will be found that the curves are generally linear, which indicates that the Freundlich adsorption isotherm is obeyed in all these cases.

FIG. 3  
Adsorption isotherms.



The curves in order from top to bottom refer respectively to  $\text{H}_2\text{SO}_4$  on Na-Deacidite; NaOH on H-Zeokrab 215; NaOH on H-Ionac-C-284; NaOH on H-Amberlite IR-100, and  $\text{H}_2\text{SO}_4$  on Na-Ionac A-293.

For the adsorption of alkali by acid forms of resins, the isotherms for Amberlite IR-100 and Zeokarb run nearly parallel, but that for Ionac C-28, has a lower slope.

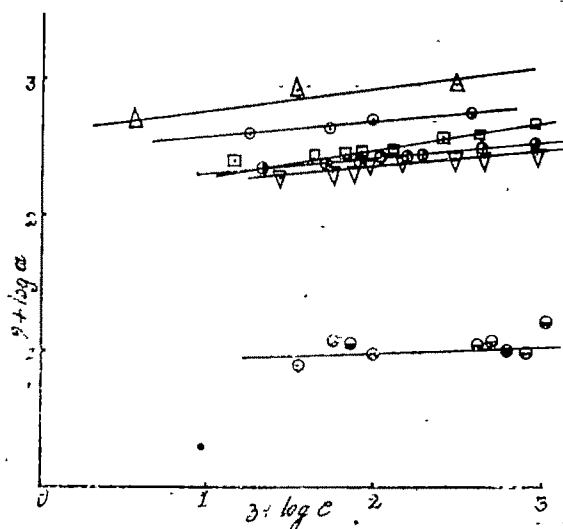
If the interaction between the acid form of a cationic resin and an alkali in solution be regarded as chemical neutralisation of the surface acid groups, the amount of alkali neutralised by the resin would correspond stoichiometrically to the number of neutralisable acidic groups and would be independent of the concentration of the alkali employed, provided that its quantity was so chosen that an excess remained at the end. Myers (*loc. cit.*) attributed the resemblance of such phenomena to an adsorption process to the disturbing effects of diffusion and reaction velocity. But in the experiments described above, sufficient time was allowed for the resin to come to equilibrium with the alkali solution, and therefore those factors do not come into play. The interaction appears to be a true adsorption process (cf. Bhatnagar *et al.*, *loc cit.*).

The similarity in the slopes of the isotherms for Zeokarb and Amberlite points to a similarity in the adsorbing nature of the two surfaces, the difference in level indicating the difference in the number of active centres. But the two resins are quite different chemically, the former being a sulphonated coal and the latter, a resin of phenol-formaldehyde type, treated with sulphite. The resemblance lies in the surface properties rather than in the chemical nature of the adsorbing groups.

The alkali adsorption curves for the acidic forms of anionic resins have a relatively small slope (Fig. 3). It would appear that here the hydrogen ions associated with the resins are more easily available for neutralisation, and consequently increase in the concentration of the alkali makes smaller difference. The isotherm would still indicate an adsorption process, possibly the adsorption of hydroxyl ions on the surface.

*Adsorption of Acids*—The isotherms for the adsorption of sulphuric acid on alkali forms of anionic resins (Fig. 4) are also typical of an adsorption process. The question is whether the acid is adsorbed molecularly, or it is an ion-exchange process. The results of the interaction of salts with the alkali forms of anionic resins throw light on this point (Table X). Alkali is liberated as a result of this interaction and potassium sulphate or phosphate liberates more alkali than the chloride. This can be regarded as the exchange of surface hydroxyl ions for the anions of the added electrolyte, and one with a higher valency has a greater capacity for displacing the hydroxyl ions. This observation supports those of Jenny (*loc. cit.*) and of Kunin and Myers (*loc. cit.*).

FIG. 4



Curves from top to bottom refer respectively to

- (a) NaOH on H-Deacidite,
- (b) NaOH on H-Ionac A-293,
- (c)  $\text{H}_2\text{SO}_4$  on Na-Zeokrab 215,
- (d)  $\text{H}_2\text{SO}_4$  on Na-Ionac C-284,
- (e)  $\text{H}_2\text{SO}_4$  on Amberlite IR 100 and
- (f) NaOH on H-Zeokrab 215

A comparison of Tables V and VI will show that sulphuric acid is adsorbed more strongly than hydrochloric acid. This is in accordance with the observation made above that sulphate ions have a greater displacing power than chloride ions.

The curves for the adsorption of acid by the alkali forms of cationic resins (Fig 2) are less steep than those for the anionic resins. Neutralisation of loosely bound alkali, coupled with adsorption of hydrogen ions, appears to be indicated.

The adsorption of sulphuric acid on the acidic form of Zeokarb presents a peculiar feature (Table IV, Fig 4.). A small but definite adsorption is noticed which, however, does not vary significantly with the concentration of acid employed.

#### *Potentiometric Titration Curves*

The titration curves for Zeokarb, Amberlite and Ionac (Fig. 1) show that all the three have a strong acid character, but the total acidities vary in the order: Ionac C-284 > Amberlite IR-100 > Zeokarb 215. The curve for Zeokarb shows a sharper inflexion than the other two, but beyond this point the curve flattens at a lower  $p_H$ , indicating a buffering effect between  $p_H$  9 and 10. Resins having sulphonic acid as the functional group are known to adsorb at low  $p_H$  values, but the shape of the titration curve points to the existence of other types of groups also, which can adsorb hydrogen ions in the alkaline region. Similarly, Amberlite appears to have a stronger buffer action than Ionac at  $p_H$  below 11.

The titration curves for anionic resins (Fig. 2) show an entirely different character. The curve for Ionac A-293 shows continuous variation of  $p_H$ , with only a slight break between  $p_H$  3 and 4, and hence resembles that of an extremely weak base. The titration curve for Deacidite resembles that of a moderately weak base, showing a short buffering range above  $p_H$  5 and an inflexion between  $p_H$  4 and 5. The total acidity of the latter is also somewhat greater than that of the former, both being calculated from the inflexion points.

#### *Exchange Capacities of Resins*

If the end-points of the titration curves indicate the complete neutralisation of the acidic or basic groups on the surface of the resins, these would also represent the total base or acid binding (or exchange) capacities of the materials. The values, so calculated, are given in Table XII. The results are expressed as milli-equivalents of acid or base bound per g. of the resin.

TABLE XII

*Base or acid binding capacities obtained from titration curves.*

Cationic resin.	Base binding capacity (m.e./g.).	Anionic resin.	Acid binding capacity (m.e./g.)
Zeokarb 215	0.833	Ionac A-293	5.0
Amberlite IR-100	1.250	Deacidite	5.83
Ionac C-284	2.083		

A reference to Table III will, however, show that the base-adsorption capacities of the three cationic resins vary in the order :

Ionac C-284 > Zeokarb 215 > Amberlite IR-100

The discrepancy is difficult to explain except by attributing to the fact that while the base adsorption figures given in Table XII correspond to  $p_H$  values between 6 and 8 of the solutions, those in Table III correspond to the highly alkaline region. It has been observed above that Zeokarb, which has the lowest base binding capacity at the point of inflexion ( $p_H$  6.5), shows base adsorption in the alkaline region, and this would explain the high value for base adsorption by Zeokarb in Table III. The titration curves for Amberlite and Ionac would similarly explain the greater base adsorption shown by the former from alkaline solutions.

It would thus appear that neither the adsorption isotherm nor the titration curve is alone sufficient to characterise the base binding properties of cationic resins. A study of both would give a more complete picture. For anionic resins, however, both appear to lead to similar results.

#### *The Adsorption of Alkaloids*

Since the isolation and separation of alkaloids promise to be a potential field of application of synthetic resins, a comparative study was made of the adsorptions of quinine, strychnine and caffeine, from solutions of their salts, on the acid forms of cation-exchange resins. The results are shown in Table XIII. The initial concentration of the alkaloid salt solution was, in each case, 0.02M.

TABLE XIII

*Adsorption of alkaloids by cationic resins.*

Alkaloid salt.	H-Zeokarb 215		H-Amberlite IR-100		H-Ionac C-284	
	Equilib. conc. of alkaloid.	Adsorption (mg./g.).	Equilib. conc. of alkaloid.	Adsorption (mg./g.).	Equilib. conc. of alkaloid.	Adsorption (mg./g.).
<b>Quinine sulphate</b>						
(in 0.02 N-H <sub>2</sub> SO <sub>4</sub> )	0.0121M	127.5	0.0187M	19.8	0.0008M	311.4
<b>Strychnine hydrochloride</b>						
(neutral soln.).	0.0090	183.8	0.0168	53.5	0.0002	331.7
Do (in 0.02 N-HCl)	0.0095	173.9	0.0176	40.1	0.0002	330.3
<b>Caffeine hydrochloride</b>						
(neutral soln.)	0.0096	100.6	0.0096	106.2	0.0110	87.4
Do (in 0.02 N-HCl)	0.0100	96.8	0.0084	112.4	0.0115	82.8



The results in Table XIII show that a resin having a high adsorptive power for one alkaloid, may not behave similarly for a different alkaloid. In Table XIV, the relative adsorptive powers of the different resins for each of the alkaloids studied have been shown, the number 1, 2 and 3 representing a descending order of magnitude.

TABLE XIV

*Relative orders of adsorption of alkaloids.*

No.	Quinine.	Strychnine	Caffeine
1	H-Ionac C-284	H-Ionac C-284	H-Amberlite IR-100
2	H-Zeokarb 215	H-Zeokarb 215	H-Zeokarb 215
3	H-Amberlite IR-100	H-Amberlite IR-100	H-Ionac C-284

The relative order of adsorption for quinine and strychnine (Table XIV) agrees with the order of base-adsorption capacities as determined by adsorption isotherms, but not with that obtained from the potentiometric titration curves. Again, from the practical point of view, one must consider the kinetics of the adsorption and the effects of grain size. Thus, it was found that, for the adsorption of quinine in ion-exchange columns, Zeokarb adsorbed the alkaloid more readily than Ionac during the percolation, although the latter has a higher adsorbing power under static equilibrium conditions.

The above studies are intended to draw attention to the complexities in the phenomena of adsorption of synthetic resins and to the various factors which need study before a proper choice of a resin can be made and the conditions established for any practical application.

The authors wish to express their thanks to Dr. U.P. Basu, D.Sc., F.N.I. for his interest in the work.

BENGAL IMMUNITY RESEARCH INSTITUTE,  
CALCUTTA.

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## STUDIES ON VITAMIN-A IN SOLUTION. PART III. INITIAL LOSS OF POTENCY AND FUNCTION OF HYDROGEN DONATING SUBSTANCE

BY U. P. BASU AND SUKHAMOY BHATTACHARYA

The loss of vitamin-A in solution may be better controlled if the substrate be previously adjuvated with suitable antioxidant. In such a function a hydrogen donating substance plays no special part when the substrate is a natural or synthetic, saturated or unsaturated glyceride or ester. The above hydrogen donating substance has no appreciable antioxygenic function.

In part II of this series (Basu and Bhattacharya, this *Journal*, 1949, **26**, 459) mention has been made of the observation that vitamin-A alcohol when dissolved in glycerides or esters, whether natural or synthetic, saturated or unsaturated, loses a portion of its potency which has been termed as "initial loss". But this initial loss was not experienced when either vitamin-A alcohol was dissolved in liquid paraffin or when vitamin-A acetate was diluted with esters, saturated or unsaturated. Attempts were made to vary the conditions of experiment so as to find out the methods by which this initial loss of potency in vitamin-A alcohol might be prevented. In course of experiments carried out for finding the mode of action of the antioxidant, it was noticed (Basu and Bhattacharya, *loc. cit.*) that oleic acid exerted a synergistic action on the antioxidant in case where the substrate was liquid paraffin. But it has now been found that oleic acid itself has practically no antioxygenic function, neither it has been found to potentiate the antioxygenic function of propyl gallate to any appreciable degree when the substrate is arachis oil, ethyl oleate or ethyl stearate. The results of all these experiments have been embodied in the present paper. The paper is based on a pending patent application.

### EXPERIMENTAL

*Studies on the Initial Loss of Potency in Vitamin-A Alcohol.*—Vitamin-A concentrate used had  $1 \times 10^6$  I.U. per g. of vitamin-A potency; *n*-propyl gallate of m.p.  $146-48^\circ$ ; oleic acid of B.P. specification; arachis oil, ethyl oleate and ethyl stearate had the characteristics described in part I of this series (Basu and Bhattacharya, *ibid.*, 1949, **26**, 419). Vitamin-A acetate was of U.S.P. reference standard quality and liquid paraffin of B.P. specification had been used in this investigation. Oleic acid and propyl gallate used were 0.21% and 0.05% respectively in all cases. Variations in the method of preparation were made and the details will be found in column (a) of Table I. Accurately weighed amounts of the above vitamin-A concentrate, which had been previously assayed for its vitamin-A potency, was dissolved in 25 c.c. of arachis oil or liquid paraffin but in the case of vitamin-A acetate, two gelatine capsules, each containing 2500 I.U. of vitamin-A per capsule, were taken into 10 g. of the substrate, ethyl oleate or ethyl stearate, and the tips of the capsules were cut off with a fine scissors. The theoretical potency of each of the preparations was calculated which will be found in column (c) in Table I. Representative sample from each of the preparations was weighed and assayed for its vitamin-A content by the method described in part I of this series (Basu and Bhattacharya, *loc. cit.*). The results of these analyses are recorded in column (b) of Table I.

*Oleic Acid as an Antioxidant.*—To ascertain any antioxygenic function of oleic

acid, vitamin-A concentrate was diluted with liquid paraffin in such a way that each gramme of the preparation contained 1100 I.U. of vitamin-A. This preparation was adjuvated with 0.21% oleic acid and was taken in an amber-coloured resistant bottle fitted with perforated cork to allow introduction of glass tubings for aeration. Pure and dry air at the rate of 4 c.c. per second was passed through the system and samples withdrawn at intervals were assayed for their vitamin-A content in the usual way. The results are recorded in the first two columns of Table II. The loss of potency of vitaminised liquid paraffin (i) without antioxidant, (ii) with antioxidant and (iii) with antioxidant and oleic acid are also shown in Table II for comparison.

#### *Synergistic Action of a Hydrogen donating Substance*

*Oleic Acid in Glyceride or Ester System.*—Oleic acid, when present with an antioxidant in vitaminised liquid paraffin system, acts as a regenerator of the bound antioxidant and as a result vitamin-A potency is better protected. This observation suggests for study the action of a hydrogen donating substance on an antioxidant when the substance is externally added to a vitaminised ester or glyceride system. Accordingly vitamin-A concentrate was dissolved in arachis oil, ethyl oleate and ethyl stearate separately. A portion (25 c.c.) of each of the preparations was fortified with 0.05% propyl gallate and another 25 c.c. portion of each was adjuvated with 0.21% oleic acid in addition to 0.05% propyl gallate. The preparations were taken in amber-coloured resistant bottles for aeration. Vitamin-A content of each was determined initially and at intervals during aeration. The results of these experiments will be found in Tables III, IV and V.

TABLE I

#### *Initial loss of potency in vitamin-A alcohol \**

Expt. No.	Details of preparation. (a)	Vitamin-A potency		
		Found (I.U./g.) (b)	Calculated (I.U./g.) (c)	Recovery.
1.	Oleic acid was mixed up with vitamin-A at first and then diluted with arachis oil.	1184	1478	80.1%
2.	Propyl gallate was mixed up with vitamin-A at first and then diluted with arachis oil.	920	1043	88.2
3.	Propyl gallate was mixed up with oleic acid, vitamin-A was added to this mixture and the mixture was finally diluted with arachis oil.	1109	1243	89.2
4.	Arachis oil was adjuvated with oleic acid and to this oil was added vitamin-A.	832	1156	71.9
5.	Arachis oil was adjuvated with propyl gallate and to this oil was added vitamin-A.	1275	1270	100.4
6.	Propyl gallate was mixed up with oleic acid, to this mixture was added arachis oil and then vitamin-A was added to this mixture.	1168	1170	99.8
7.	Vitamin-A was dissolved in liquid paraffin.	1160	1155	100.4
8.	Vitamin-A acetate was dissolved in ethyl oleate.	496	500	99.2
9.	Vitamin-A acetate was dissolved in ethyl stearate.	503	500	100.6

\* Oleic acid in the system is 0.21% and propyl gallate, 0.05% in all cases, where they are present.

TABLE II

*Oleic acid as an antioxidant.*

Substrate—Liquid paraffin.

Aerated for	With 0.21% oleic acid.		Without antioxidant.		With antioxidant.		With antioxidant and oleic acid.	
	Vitamin-A (I.U./g)	% Loss of vitamin-A.	Vitamin-A (I.U./g.)	% Loss of vitamin-A.	Vitamin-A (I.U./g.)	% Loss of vitamin-A	Vitamin-A (I.U./g)	% Loss of vitamin-A
0	1100	0	1100	0	1100	0	1100	0
87 hrs.	495	55.0 <sup>1</sup>	512	53.5	658	40.2	773	29.7
142	275	75.0	305	72.3	620	43.7	755	31.4
190	200	81.8	222	79.8	610	44.6	750	31.8

TABLE III\*

*Synergistic action of oleic acid.*

Substrate—Arachis oil.

Aerated for	With antioxidant		With antioxidant and oleic acid	
	Vitamin-A (I.U./g.)	% Loss of vitamin-A.	Vitamin-A (I.U./g.)	% Loss of vitamin-A.
0	1280	0	1280	0
40 hrs.	997	22.1	—	—
54	—	—	1024	20.0
75	—	—	983	23.2
80	939	26.6	—	—
150	—	—	925	27.7
165	851	33.5	—	—

\* Oleic acid in the systems is 0.21% and antioxidant, 0.05% in all cases, where they are present.

TABLE IV\*

*Synergistic action of oleic acid.*

Substrate—Ethyl oleate.

Aerated for	With antioxidant		With antioxidant and oleic acid	
	Vitamin-A (I.U./g.)	% Loss of vitamin-A.	Vitamin-A (I.U./g)	% Loss of vitamin-A.
0	1194	0	1194	0
58 hrs.	1053	11.8	992	16.9
135	...	...	885	25.9
142	855	28.4	...	...
188	...	...	777	34.9
190	714	40.2	...	...

\* Oleic acid in the systems is 0.21% and antioxidant, 0.05% in all cases, where they are present.

TABLE V \*

*Synergistic action of oleic acid.*

Substrate—Ethyl stearate.

Aerated for	With antioxidant		With antioxidant and oleic acid	
	Vitamin A (I.U./g.)	% Loss of vitamin-A.	Vitamin-A (I.U./g.)	% Loss of vitamin-A.
0	1229	0	1229	0
47 hrs	1113	9.4	..	...
54	...	..	1060	13.7
96	1022	16.8	.	...
128	...	...	972	20.9
158	864	29.7	...	...
180	.	...	803	34.0

\* Oleic acid in the systems is 0.21% and antioxidant, 0.05% in all cases, where they are present.

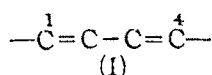
## DISCUSSION

From the results of the experiment Nos. 1 to 3 of Table I it will be found that when oleic acid or propyl gallate, either individually or both combined at a time, is admixed with vitamin-A alcohol initially and then diluted with arachis oil, the vitamin-A alcohol loses from 10.8 to 19.9% of its potency. The system of arachis oil, when initially adjuvated with oleic acid and then with vitamin-A, loses 28.1% of the calculated vitamin-A potency (cf. Expt. No. 4, Table I). But when the archis oil is mixed up with antioxidant initially and then vitamin-A alcohol is added, the preparation retains all its vitamin-A activity (cf. Expt. No. 5, Table I). Addition of oleic acid and antioxidant to the oil and then vitamin-A also keeps the vitamin-A potency to the same degree. In expt. Nos. 7 to 9 vitamin-A alcohol, when dissolved in liquid paraffin or vitamin-A acetate when incorporated in esters, saturated or unsaturated, does not lose any vitamin-A activity.

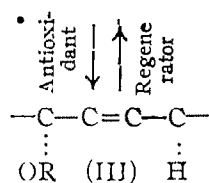
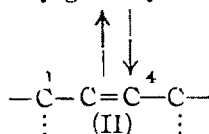
From these results it appears that the peroxide-like compounds of the substrate are responsible for the initial loss of potency of vitamin-A alcohol. The incorporation of an antioxidant in the oil, prior to the addition of vitamin-A, may form a complex with the peroxide-like body of the oil to remove it from the phase of reaction and thereby prevent the destruction of vitamin-A molecule. But if the antioxidant is adjuvated after the vitamin-A has been added to oil, the peroxide of the oil, already present, may cause deterioration of the vitamin-A molecule. Then the antioxidant would only function to prevent any further formation of peroxide (cf. Basu and Bhattacharya, *loc. cit.*).

Liquid paraffin having practically no peroxide-like compound does not affect the vitamin-A molecule and probably for this reason vitamin-A activity is not initially altered when it is dissolved in paraffin oil even without the presence of any antioxidant. It has been mentioned in part II of this series (*loc. cit.*) that the replacement of the mobile hydrogen atom of vitamin-A molecule by esterification tends to lower its prototropic change and consequently its susceptibility to receive an electronic charge. It is most probably for this reason that the peroxide, already formed in the esters (vide Expts. 8 and 9, Table I) would not so readily react with the vitamin-A acetate, and consequently, the initial loss of vitamin-A potency is not noticed in ethyl oleate or ethyl stearate in absence of any antioxidant.

From the second and third columns of Table II it may be seen that vitamin-A in liquid paraffin, when adjuvated with 0.21% oleic acid, loses its potency to the extent of 81.8% in 190 hours' aeration, while the same system without the presence of any antioxidant loses 79.8% in the same period of time. Thus, oleic acid itself seems to play no antioxygenic function and does not tend to react with the conjugated double bonded system as present in the vitamin-A molecule. That the function of oleic acid is not to act as an antioxidant but to potentiate the antioxidant in its protecting power of vitamin-A by regenerating the antioxidant and vitamin-A molecule from the complex of the type III, appears to be further substantiated from the results as recorded in Table II (vide columns 3, 7 and 9). The mechanism of the reaction in conjugated double bonded system of vitamin-A molecule may be represented in short as follows:—



Conjugated system



From Tables III, IV and V it will be seen that oleic acid, a hydrogen donating substance, when externally added in addition to antioxidant to the ester or glyceride systems containing vitamin-A, shows little or practically no synergistic action on the antioxidant. The incipient formation of a free acid in the ester or glyceride may be sufficient to regenerate the antioxidant from the complex of type III and any additional free hydrogen donating substance is most probably not offering any special advantage in this type of systems (cf. Basu and Bhattacharya, *loc. cit.*).

## CONCLUSION

The initial loss of potency of vitamin-A, when dissolved in esters or glycerides, may be prevented by the incorporation of an antioxidant to the substrates in the first instance and then adding the vitamin-A concentrate. The antioxidant combines with the peroxide-like compounds of the substrates to remove them from the phase of reaction and thus prevents those peroxides to act on vitamin-A molecule.

A hydrogen donating substance, e.g., oleic acid itself does not play the part of an antioxidant but acts as a synergistic agent on the antioxidant.

Such hydrogen donating substance, when present in an ester or glyceride system in addition to antioxidant, does not show any special effect. The incipient formation of a free acid in these systems is sufficient to act as a synergistic agent.

BENGAL IMMUNITY RESEARCH INSTITUTE,  
CALCUTTA.

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## ON THE KINETICS OF LONG CHAIN QUATERNARY SALT FORMATION\*

BY SUSHIL KUMAR MUKHERJEE AND SANTI R. PALIT

A new method has been developed to follow the kinetics of Menshutkin reaction by direct potentiometric titration of the disappearing base in non-aqueous medium. The method has been applied to study long chain quaternary salt formation. The reaction is found to be bimolecular running at a speed of the same order as that for lower halides under similar conditions. The solvent effect is also found to be similar to the previously found effect in the case of lower halides.

The rate of formation of quaternary salts by the reaction between an alkyl halide and a tertiary amine, which is some times called Menshutkin reaction, has been measured for a number of amines and halides under different conditions (Bell, *Ann. Rep. Chem. Soc.*, 1939, **36**, 82; Richardson and Soper, *J. Chem. Soc.*, 1929, 1873). However, there seems to be no study when either the amine or the halide is a long chain compound of soap-like length ( $C_{12}$  to  $C_{18}$ ) and hence, the compound formed is a surface-active agent.

This may probably be ascribed to the fact that the hitherto used methods of following such reaction are inapplicable in this case. The long chain quaternary salts are fairly well soluble in non-polar solvents and hence it is not possible to apply the original precipitation and weighing method of Menshutkin (*Z. physikal. Chem.*, 1890, **6**, 41). Neither it is possible to extract out ionisable halide with water and titrate it subsequently, as done by most later workers (cf. Pickels and Hinshelwood, *J. Chem. Soc.*, 1936, 1353; Edwards, *Trans. Faraday Soc.*, 1937, **33**, 1894) or extract out the excess base with excess of dilute sulphuric acid (Baker and Nathan, *J. Chem. Soc.*, 1935, 519) because these surface-active agents form emulsion in presence of water.

This reaction, however, is of interest because many of these compounds, for example, cetyl pyridinium chloride, cetyl trimethylammonium bromide, octadecyl dimethylbenzylammonium chloride, etc., which are usually manufactured by such a reaction, have lately assumed great technical importance owing to their surface activity, germicidal power and other properties. We have undertaken a systematic study of the kinetics of this type of reaction and this communication is to make a preliminary report of our work.

### EXPERIMENTAL

Our experimental method has been a direct and straightforward one and is different from that of all workers in this field. Since the reaction between, say, cetyl bromide and pyridine,



\* Contribution No. 24 from the Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta-12).



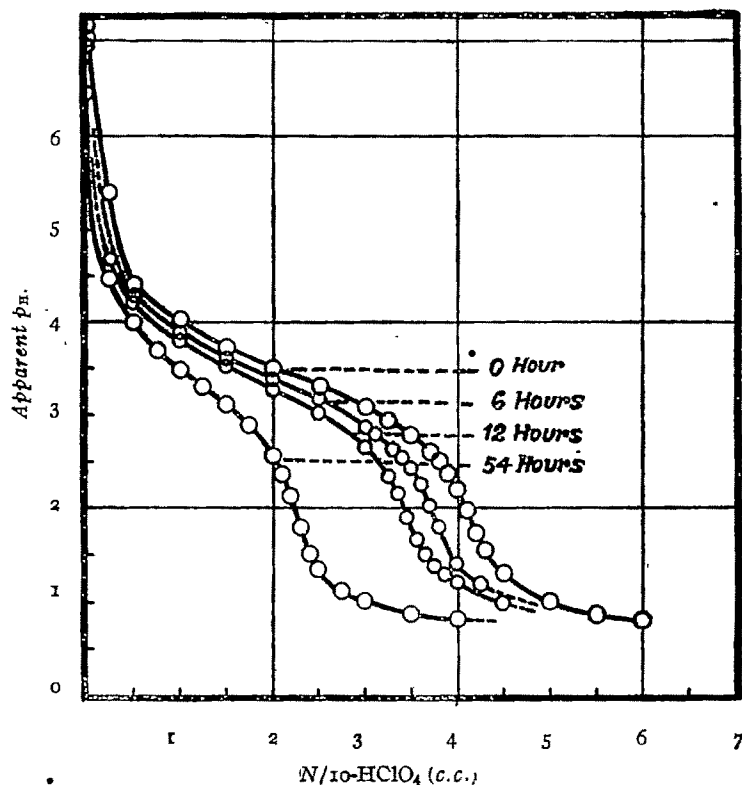
involves a disappearance of the base, pyridine, with the progress of the reaction, the reaction has been followed by directly titrating the mixtures with acid after definite intervals. The difficulty of accurately titrating such weak base as pyridine, specially in presence of organic solvents, has been solved by taking help of the method recently developed by one of us (Palit, *Ind. Eng. Chem., Anal. Ed.*, 1946, 18, 246; cf. Green, *J. Amer. Pharm. Assoc.*, 1948, 47, 240; Siggia, "Quantitative Organic Analysis via Functional Groups", John Willy & Sons, pp. 21,69) for titrating very weak bases.

The reaction mixture (10 c.c.) which was  $N/20$  with respect to both the base and the halide were sealed in pyrex glass ampules in vacuum by cooling in liquid air and evacuating. These ampules were heated in an oil thermostat maintained at constant temperature to  $\pm 0.1^\circ$  for definite periods. The ampules were broken and the contents of each was dissolved in 20 c.c. of glycol-isopropyl mixtures and was titrated potentiometrically using glass electrode against decinormal perchloric acid in the same solvent.

The result of a typical run is shown in Fig. 1 and some data in Table I, where  $k_2$  values are given without correction for expansion of the solvent medium. It will be observed from Fig. 1 that the reaction is easily followed by our technique and the data quoted in Table I show that the reaction is a bimolecular one proceeding smoothly

Fig. 1

*Disappearance of pyridine ( $N/20$ ) with progress of reaction with bromide ( $N/20$ ) in methyl ethyl ketone as shown by potentiometric titration in glycol isopropyl alcohol medium.*



up to well above 50% conversion without any appreciable change in the kinetics. These results further show that the solvent effect for these long chain reactions is essentially of the same type as shown by similar reactions with shorter chain compounds. This seems to indicate that the reaction mechanism is basically similar in both cases. Palit (*J. Org. Chem.*, 1947, **12**, 752) has postulated a possible mechanism for the solvent effect of this type of reactions according to which this type of reactions is slowest in perfectly neutral solvents and is accelerated by the acidity (electron accepting power) or basicity of solvents, the acidity of solvents playing a stronger part. It was deduced that under identical conditions  $k_{\text{CHCl}_3} > k_{\text{CCl}_4}$  and  $k_{\text{benzene}} > k_{\text{cyclohexane}}$ . Our results agree with the above expectation as also with the expected higher speed in alcohol owing to the comparatively high acidity of its hydroxylic hydrogen.

TABLE I

Bimolecular constant,  $k_2$  (100°).

Solvent.	Reaction time.	% Reacted.	$k_2$ (mol <sup>-1</sup> min <sup>-1</sup> litre)	Mean $k_2$ .
Reaction : $\text{C}_{16}\text{H}_{33}\text{Br} + \text{C}_5\text{H}_5\text{N} \rightarrow [\text{C}_{16}\text{H}_{33}.\text{NC}_5\text{H}_5]^+ \text{Br}^-$				
$\text{CCl}_4$	96 hrs.	7.78	0.000031	0.000032
	247	20.35	0.000034	
$\text{CHCl}_3$	29	28.05	0.00046	0.00041
	48	35.84	0.00040	
	100	52.72	0.00038	
$\text{CH}_3\text{COC}_2\text{H}_5$	6	9.26	0.00035	0.00052
	12	16.34	0.00053	
	54	45.12	0.00049	
$n\text{-C}_4\text{H}_9\text{OH}$	12	34.34	0.00146	0.00147
	48	67.19	0.00147	
Reaction : $\text{C}_{12}\text{H}_{25}\text{Br} + \text{C}_5\text{H}_5\text{N} \rightarrow [\text{C}_{12}\text{H}_{25}.\text{NC}_5\text{H}_5]^+ \text{Br}^-$				
$\text{CCl}_4$	37	2.09	0.000020	0.000022
	158	9.42	0.000023	
	247	14.39	0.000023	
$\text{CHCl}_3$	29	23.7	0.00033	0.00032
	48	33.64	0.00033	
	100	49.52	0.00031	
$\text{CH}_3\text{COC}_2\text{H}_5$	6	8.75	0.00056	0.00054
	12	15.91	0.00055	
	54	43.76	0.00051	
$n\text{-C}_4\text{H}_9\text{OH}$	12	31.12	0.00126	0.00127
	21	46.07	0.00136	
	48	63.48	0.00121	
Benzene	138	12.37	0.000030	0.000028
	264	19.30	0.000027	
Do (99.8°)	$\text{C}_3\text{H}_7\text{Br} + \text{C}_5\text{H}_5\text{N}$ (pyridine) $\rightarrow [\text{C}_2\text{H}_5\text{NC}_5\text{H}_5]^+ \text{Br}^-$		$24.9 \times 10^{-6}$	
Do (99.8°)	$n\text{-C}_3\text{H}_7\text{Br} + \text{C}_5\text{H}_5\text{N}$ (pyridine) $\rightarrow [\text{C}_3\text{H}_7\text{NC}_5\text{H}_5]^+ \text{Br}^-$		$10.1 \times 10^{-6}$	

In the same table we have compared our data with a few similar data for lower alkyl bromides and pyridine. It will be observed that under identical conditions the

reaction studied by us proceeds with a speed of the same order as for the lower alkyl bromides. For example, in benzene our  $k_2$  value for dodecyl bromide is  $30 \times 10^{-6}$  (corrected for expansion of solvent) against  $24.9 \times 10^{-6}$  for ethyl bromide as given by Pickels and Hinshelwood (*loc. cit.*). Quantitatively speaking, the longer chains run the reaction at a higher speed. Pickels and Hinshelwood observed the speed to decrease from  $24.9 \times 10^{-6}$  to  $10.1 \times 10^{-6}$  as they pass from ethyl to propyl bromide. We, however, find the speed to increase (except in methyl ethyl ketone) as we pass from dodecyl to hexadecyl bromide. It is possible that as we pass from methyl upwards the speed gradually drops and again begins to increase as we approach the soap-type length. It is difficult to discern from these preliminary results what part the inductive effect of the alkyl groups is playing in influencing the speed, but it seems, *a priori*, that this increase of speed is more likely due to a decrease in the heat of activation than to an increase in the  $PZ$  factor, because the entropy factor for such long chains will be unfavourable for reaction as oriented collisions will be necessary for the reaction. Work is in progress to thoroughly investigate the above points.

DEPARTMENT OF PHYSICAL CHEMISTRY,  
INDIAN ASSOCIATION FOR THE CULTIVATION  
OF SCIENCE, CALCUTTA.

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## KINETICS OF HALOGENATION OF FATTY ACIDS. PART II. BROMINATION OF ACETIC ACID\*

BY MIHIR NATH DAS AND SANTI R. PALIT

The kinetics of bromination of sodium acetate in glacial acetic acid has been measured at 35° and 25° in presence of excess of sodium bromide. The reaction is found to be bimolecular, the bimolecular constant  $k_2$  having the mean value 1.90 litre/mole min<sup>-1</sup> at 35° and at bromide concentrations 0.109 to 0.168M.

The energy of activation is of the order of 15,600 cal./mole. The PZ factor has got almost the normal value of 10<sup>11</sup>.

Using different alkali acetates, the speeds are found to be in the order : K > Na > Li.

Water strongly accelerates the reaction, the speed rising progressively with increasing proportions of water to a maximum, after which the speed falls off. In acetic acid containing about 50% or more of water, the bimolecular nature of the reaction is no longer evident. In pure water, practically no reaction is found to occur.

It is suggested that the reaction occurs through the attack of the positive end of the polarised bromine molecule on the  $\alpha$  carbon atom which becomes activated by an inductive mechanism.

In a previous paper (Das and Palit, this *Journal*, 1949, **26**, 322) we have reported the results obtained from a preliminary study of the reaction of iodine with sodium acetate in glacial acetic acid medium. It is reported therein, as also in an earlier note (Das, *Science & Culture*, 1948, **14**, 165) that bromine too reacts with the same system and other similar systems, the reaction being much faster than with iodine. The present paper deals with the preliminary results of the kinetics of the bromination of sodium acetate in glacial acetic acid medium.

Bromine is practically without any action on saturated aliphatic acids at the ordinary temperature. Lapworth (*J. Chem. Soc.*, 1904, **88**, 30) reports that bromine scarcely acts on acetic acid even at its boiling point, and the reaction is catalysed by HCl or HBr. Watson (*ibid.*, 1925, 2067) studied the bromination of acetic, propionic and *n*-butyric acids at 100° in presence and absence of catalysts. The reaction is rather slow even at such a high temperature in absence of catalyst, and the course of the reaction is kinetically quite complex and difficult of elucidation and indicates autocatalysis by the HBr formed. The bromination is catalysed by HBr and HCl, the action of the halogen acids being specific and not involving any general acid-catalysis. Acetic anhydride, various acid chlorides and especially acid bromides, if added in excess of the water present in the acid, act as powerful catalysts at 100°. The reaction rate is proportional to the first power of the concentration of bromine as well as that of the catalyst. No base-catalysis has so far been reported for the bromination of aliphatic acids. On the contrary, Watson (*J. Chem. Soc.*, 1927, 2458, 3065) observed that the bromination of acetic anhydride was strongly retarded by quinoline, and to a lesser extent, by sodium acetate. Other bases like pyridine, isoquinoline,

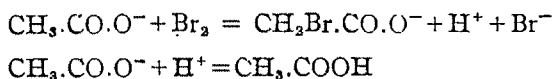
\*Contribution No. 23 from the Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta-12.

aniline, and different aliphatic amines and  $\text{NH}_4$ -acetate are less powerful inhibitors. The inhibitory action of sodium acetate is of particular interest to us, when viewed in the light of the reaction forming the subject of our present study.

### EXPERIMENTAL

The methods of preparation of materials were similar to those described in our previous communication (*loc. cit.*). Experimental procedure for kinetic measurements was the same as described therein. Laboratory reagent bromine was used without any special purification. Acetate was estimated as follows. The acetic acid solution was evaporated on a water-bath, the residue taken up with glycol-isopropyl alcohol mixture and titrated with standard  $\text{HClO}_4$  solution in the same mixed solvent, with thymol blue as indicator. This method, originally devised by one of the authors (Palit, *Ind. Eng. Chem., Anal. Ed.*, 1946, 18, 246) has been found to be quite suitable for estimation of acetate (cf. Green, *J. Amer. Pharm. Assoc.*, 1948, 37, 240).

*Reaction Kinetics.*—From our results to be reported the reaction appears to take the course,



In the first step, one acetate ion undergoes bromination, liberating a molecule of  $\text{HBr}$ , which being a strong acid neutralises a second acetate ion, the latter being a strong base in glacial acetic acid medium. Thus, with every molecule of bromine, two acetate ions take part in the overall reaction. The second step involving the neutralisation of a strong base with a strong acid is naturally an instantaneous process, so that the first step must be the rate determining factor. Now, the instantaneous rate of reaction is given by

$$\frac{dx}{dt} = k_2[\text{Ac}][\text{Br}_2] \quad \dots \quad \dots \quad \dots \quad (1)$$

where  $x$  denotes the amount of  $\text{Br}_2$  consumed. The tribromide equilibrium is defined by the equation,

$$K = \frac{[\text{Br}_2][\text{Br}^-]}{[\text{Br}_3^-]} \quad \dots \quad \dots \quad \dots \quad (2)$$

Let  $a$  and  $b$  denote the initial concentrations of bromine and acetate respectively. Then, the total titratable bromine at any time  $t$  is given by

$$a - x = [\text{Br}_2] + [\text{Br}_3^-] \quad \dots \quad \dots \quad \dots \quad (3)$$

Combining equations (2) and (3), the concentration of free bromine at any time  $t$  is given by

$$\text{Br}_2 = \frac{(a-x)K}{K + [\text{Br}^-]} \quad \dots \quad \dots \quad \dots \quad (4)$$

Now, the total bromide at any stage is given by  $x = [\text{Br}^-] + [\text{Br}_3^-]$  ... .. (5)

Combining this equation with (2) and (4) and solving the resulting quadratic equation, the concentration of free bromide at any state is given by

$$[\text{Br}^-] = \frac{2x - a - K + \sqrt{(-2x + a + K)^2 + 4Kx}}{2} \quad \dots \quad (6)$$

Substituting this value of  $[\text{Br}^-]$  in (4), we may obtain the concentration of free bromine at any stage of the reaction.

Thus, the kinetic equation (1) assumes the form

$$\frac{dx}{dt} = \frac{k_2 (b - 2x) (a - x) K}{K + [\text{Br}^-]} \quad \dots \quad (7)$$

where  $[\text{Br}^-]$  has got the value given by equation (6) and  $K$  is the equilibrium constant given by equation (2). This equation, however, involves enormous calculations which can be simplified to a great extent by carrying out the reaction in presence of bromide added in excess (cf. Griffith and Mackeown, *Trans. Faraday Soc.*, 1932, 28, 752; Nozaki and Ogg, *J. Amer. Chem. Soc.*, 1942 64, 697). If  $c$  represents the concentration of added bromide, it can be shown that free bromide at any stage is given by

$$[\text{Br}^-] = \frac{1}{2} \left\{ (c + 2x - a - K) + \sqrt{(-c - 2x + a + K)^2 + 4K(c + x)} \right\} \quad \dots \quad (8)$$

Now, if  $x$  is small in comparison with  $c$ , from the above equation it may be seen that  $[\text{Br}^-]$  remains practically constant throughout the reaction. Hence, free bromine at any instant is given by equation (4) as

$$[\text{Br}_2] = \frac{(a - x)K}{K + [\text{Br}^-]} = \alpha (a - x) \quad \dots \quad (9)$$

where  $\alpha$  is a constant because  $[\text{Br}^-]$  is constant under the conditions of experiment, i. e., at any instant is proportional to the total titratable bromine present. Under these conditions equation (7) assumes the form

$$\frac{dx}{dt} = \alpha k_2 (b - 2x) (a - x) \quad \dots \quad (10)$$

When  $b = 2a$ , this being the case in most of our experiments, the above equation reduces to the form

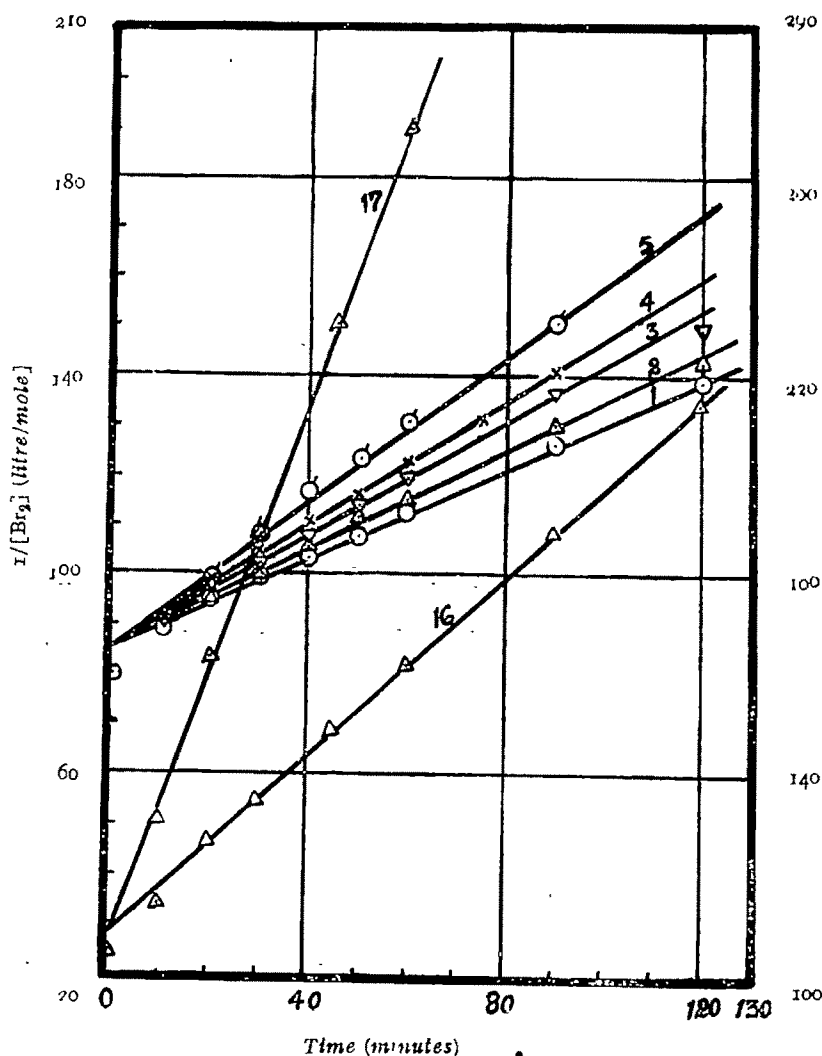
$$\frac{dx}{dt} = 2\alpha k_2 (a - x)^2 \quad \dots \quad (11)$$

On integration we have,

$$\frac{1}{a - x} = 2\alpha k_2 t + c' \quad \dots \quad (12)$$

Thus, the reciprocal of the total bromine concentration, when plotted against  $t$ , will give a straight line, the slope of which is  $2\alpha k_2$ , and hence the bimolecular constant  $k_2$  may be calculated. Experimental results were found to be in excellent agreement with this equation. The straight lines so obtained do not, however, pass through the zero time point. Some of the typical results are represented (Fig. 1) and the corresponding data in the following tables.

FIG. 1



The figures on the curves refer to respective expt. Nos. as represented in the relevant tables. Ordinates for the curves 1-5 are shown on the left and those for 16 and 17 on the right.

**Tribromide Equilibrium in Glacial Acetic Acid.**—As would be seen from above, a knowledge of the tribromide equilibrium constant in glacial acetic acid ( $K$ ) is essential to interpret the kinetic data. This was studied by Nozaki and Ogg (*loc. cit.*) and they have given a series of values for  $K$  at different temperatures and ionic strengths. From these data we have calculated the values of  $K$  at  $35^\circ$  and  $25^\circ$  by the application of Van't Hoff's equation, the validity of which for this particular case was also demonstrated by the same workers (*loc. cit.*). The values of  $K$  at ionic strength, close to our experimental conditions thus obtained, are given below and have been utilised in our calculations.

$$K_{35^\circ} = 2.2 \times 10^{-2}$$

$$K_{25^\circ} = 1.49 \times 10^{-2}$$

TABLE I

*Change of thiosulphate titre (N/100) in c. c. for 5 c. c. of reaction mixture.*

Temp. = 35°. Initial conc. of bromine (a) = 0.0125M. Initial conc. of Na acetate (b) = 0.025M. Concentration of added bromide (c) is given for each run at the head of the corresponding column in moles/litre.

	Experiment number				
	1	2	3	4	5
	c = 0.168	0.153	0.138	0.123	0.109
Time.	Titre	Titre	Titre	Titre	Titre.
0 min.	12.50 c.c.	12.50 c.c.	12.50 c.c.	12.50 c.c.	12.50 c.c.
10	11.20	10.82	11.02	10.92	—
20	10.56	10.50	10.18	10.14	10.10
30	10.04	9.98	9.80	9.54	9.20
40	9.66	9.42	9.24	9.02	8.52
50	9.24	8.92	8.76	8.60	8.10
60	8.86	8.66	8.34	8.12	7.68
90	7.90	7.66	7.32	7.10	6.62
120	7.20	7.02	6.64	—	—

*The Bimolecular Constant.*—On carrying out the reaction at different concentrations of bromide running up to 0.26M, the values of  $k_2$ , calculated as above, were found to lie in the range 1.41–2.28 (litre/mole) min<sup>-1</sup> units at 35°. This divergence in the values obtained might be due to the variable amounts of water likely to be associated with the different samples of acetic acid used in the experiments, as water strongly accelerates the reaction. Using a highly purified sample of acetic acid, the data shown in Table I were obtained, and the determination of  $k_2$  from these results gave the following values, which are found to be fairly concordant and independent of bromide concentration,

TABLE II

*Values of the bimolecular constant ( $k_2$ ) at 35°.*

Expt. No.	Conc. of bromide	$ak_2$	$k_2$ (litre/mole) min <sup>-1</sup>	Mean value of $k_2$
1	0.168M	0.222	1.85	1.90
2	0.153	0.244	1.88	
3	0.138	0.281	1.94	
4	0.123	0.304	1.92	
5	0.109	0.333	1.91	
5-1737P-4.				



*Effect of Temperature.*—The reaction was studied at 35° and 25° in presence of similar concentrations of bromide. At the lower temperature, there is an apparent period of induction, as noticed in the case of iodination as well. The reason for this is not understood. From the value of the ratio  $k_{35}/k_{25}$ , the activation energy was calculated and found to be of the order of 15,600 cal. This may be compared with the value of 25,000 cal. obtained for iodination. In Table III are given the results of two typical runs at 25°, together with two runs at 35°, for comparison. Values of  $k_2$  at 25° are found to be 0.94–1.00 (litre/mole) min<sup>-1</sup> units. The PZ factor calculated from these results is found to be of the order of 10<sup>11</sup>, which appears to be almost a normal value.

TABLE III  
*Effect of temperature.*

		Experiment No.			
		6	7	8	9
		35°	Temperature 25°	35°	25°
		$a = 0.025M$	0.0238M	0.0125M	0.0125M
		$b = 0.05$	0.05	0.025	0.025
		$c = 0.260$	0.260	0.133	0.097
Time.	Titre	Titre	Titre	Titre	Titre
0 min.	25.00 c.c.	23.80 c.c.	12.50 c.c.	12.50 c.c.	
10	21.58	—	11.70	—	
20	19.80	21.75	10.85	12.40	
30	18.22	21.40	10.20	12.06	
45	16.48	20.35	9.25	11.44	
60	15.20	19.35	8.30	11.04	
75	—	18.70	—	—	
90	13.02	18.10	7.30	10.00	
105	—	17.35	—	—	
120	11.72	16.80	6.50	9.54	

*Effect of Different Alkali Acetates.*—The reaction was also carried out with potassium and lithium acetates to compare the effects of the different alkali metals. Due to the very sparing solubility of potassium bromide in glacial acetic acid, the reaction was studied for all the three alkali acetates, in absence of any added bromide (Table IV). The speeds were found to lie in the order: K > Na > Li. The difference between Na and Li, however, is not so pronounced. An exactly similar effect was observed by us for the corresponding reactions with iodine. This order, as reported earlier, is also the order of the conductivities of these salts in glacial acetic acid medium (Kolthoff and Wilman, *J. Amer. Chem. Soc.*, 1934, 56, 1014).

TABLE IV

*Effect of different alkali metals.*

Temp. = 35°. Change of thiosulphate titre with time.  $a = [\text{Br}_2] = 0.0125M$ ,  
 $b = [\text{Ac}] = 0.025M$ .

Time.	Experiment No.		
	10	11	12
	K.	Alkali metal Na.	Li.
	Titre	Titre	Titre
0 min.	12.50 c.c.	12.50 c.c.	12.50 c.c.
5	9.60	10.80	10.60
10	8.45	9.90	10.00
20	7.15	8.80	9.15
30	6.25	8.10	8.50
45	5.50	7.20	7.90
60	5.00	6.70	7.35

*Effect of Water.*—Water strongly accelerates the reaction and the speed rapidly increases with increasing proportions of water. In Table V are shown some typical results obtained in aqueous acetic acid media containing varying proportions of water in presence and absence of bromides.

TABLE V

*Effect of water.*

Temp = 35°.

Experiment No.

Time.	13	14	15	16	17
	Water contents in acetic acid (% by volume).				
	0%	10%	50%	8%	20%
	$a = 0.0125M$	$0.0125M$	$0.0125M$	$0.0096M$	$0.0096M$
	$b = 0.0125$	$0.0125$	$0.025$	$0.0192$	$0.0192$
	$c = \text{Nil}$	Nil	Nil	$0.201$	$0.201$
	Titre	Titre	Titre	Titre	Titre
0 min.	12.50 c.c.	12.50 c.c.	12.50 c.c.	9.63 c.c.	9.63 c.c.
5	11.18	9.52	3.60	—	—
10	10.40	8.50	2.12	8.75	7.66
20	9.20	7.68	—	7.90	6.10
30	8.78	7.12	—	7.40	5.30
45	8.20	6.80	0.45	6.70	4.34
60	8.00	6.52	—	6.16	3.70
90	6.50	6.12	—	5.30	2.76
120	—	5.82	—	4.66	—

In pure aqueous medium, as also in 5% aqueous acetic acid, very little reaction is found to occur. In acetic acid containing about 50% or higher proportion of water, the bimolecular nature of the reaction (in presence of excess bromide) is no longer evident, and no mathematical relationship could be found out to represent the kinetic results. The kinetics of the reaction in such aqueous acetic acid media are still under investigation.

The reaction was followed kinetically at 35° in acetic acid containing 8% and 20% water respectively at 0.201*M* bromide concentration (Table V, Expt. No. 16 & 17), and the values of  $ak_2$  were found out graphically as before (Fig. 1; curves 16 and 17). To determine  $k_2$ , the values of the tribromide equilibrium constant ( $K$ ) in the different media are necessary. From the values of  $K_{18}$  given by Jones (*J. Chem. Soc.*, 1911, 99, 392) for aqueous acetic acid media, it is found that  $K$  does not change enormously, unless the water content is very high. Assuming a similar effect to occur at 35°, the values of  $K_{35}$  were roughly calculated for aqueous acetic acid containing 8% and 20% water. The approximate values of  $k_2$  were then calculated on this basis, which are tabulated below (Table VI).

TABLE VI

*Values of  $k_2$  in aqueous acetic acid.*

Expt. No.	% Water in acetic acid (by volume).	$K$ (approx.).	$ak_2$	$k_2$ (approx.) (litre/mole) min <sup>-1</sup> .
16	8	0.027	0.437	3.6
17	20	0.035	1.36	8.5

The accelerating effect of water is, in part, due to an increase in the value of  $K$  in aqueous acetic acid media, implying a higher concentration of free  $\text{Br}_2$ , but this factor is too small to account for the enhanced speed, as evident from the above table.

The higher speed of the reaction in water might be thought to arise from a greater dissociation of the acetate caused by the addition of water, but this is not the whole story as shown by the fact that practically no reaction occurs in pure water. It is interesting to note in this connection that bromine is found to react very slowly with aqueous acetic acid containing 8 to 20 % water even in absence of any added acetate.

*Bromination and Iodination compared.*—The two reactions present many points of similarity between themselves. Both the reactions are kinetically bimolecular, but bromination is more than hundred times faster than the reaction with iodine. Both reactions are accelerated by water and the relative effects of different alkali metals are also similar in both the cases. The most important difference between the two reactions, however, lies in the fact that whereas bromination goes to completion, in iodination, an apparent state of equilibrium is attained where the greater part of iodine remains unchanged. Thus, using even a molar concentration of acetate with as low as 0.0125*M* iodine, the reaction proceeds less than half-way. In bromination, on the other hand, with the same concentration (0.0125*M*) of the halogen, 0.025*M* acetate is sufficient to carry the reaction to completion in less than 96 hours. With higher con-

centrations of acetate, the reaction is naturally complete in a shorter period. Thus, no back-reaction being involved here, the reaction with bromine, unlike that with iodine, is more amenable to a critical kinetic study.

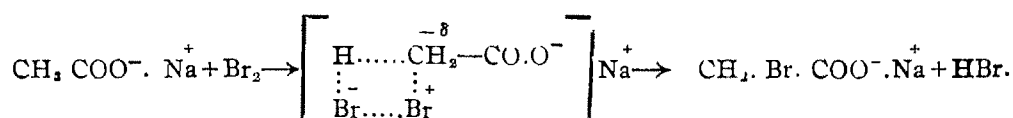
There is another important point to note in connection with the bromination reaction. According to the course of the reaction proposed by us, for each molecule of bromine, two molecules of sodium acetate take part in the overall reaction. Hence, if we start with equimolecular proportions of both the reactants, only half of the bromine should be consumed. In fact, about half the bromine was found to react in course of a few hours. But, on keeping the reaction mixture for several days, the reaction was found to proceed fairly beyond the half-value stage. This is presumably due to further bromination of the monobromoacetate first formed, the speed of which must be very slow with respect to that of the primary reaction, as otherwise we would not have obtained such consistent straight lines as previously reported (Fig. 1).

It may be mentioned in this connection, that various workers have studied the kinetics of many reactions involving bromine and iodine, in presence of acetate buffers and also using acetate as a catalyst (Bell and Lidwell, *Proc. Roy. Soc.*, 1940, **A**, 176, 88; Pederson, *J. Phys. Chem.*, 1934, **38**, 601, 999; Nozaki and Ogg, *loc. cit.* Dawson *et al.*, *J. Chem. Soc.*, 1926, 2282; 1928, 2844; 1929, 1884, etc.). These reactions were carried out in different media like water, glacial acetic acid and also aqueous acetic acid. No account was, however, taken of any reaction that might occur between the halogen and the acetate added, and naturally there is every reason to be sceptic about the reliability of the results obtained by them. The reaction of the acetate with iodine is very slow and may introduce only a small error, but with bromine in glacial as well as in aqueous acetic acid medium the reaction is fairly fast, faster than many of the common bromination reactions, and hence, the discrepancy likely to be associated with their results can hardly be ignored as negligible.

*Mechanism.*—Carbonyl compounds are, in general, easily susceptible to halogen substitution, and the reaction usually proceeds through a tautomeric mechanism. This typical property of the carbonyl group is, however, absent in free carboxylic acids, due to structural differences, which we have discussed in our previous paper. Silver, mercury and thallium salts of carboxylic acids are known to react with halogens giving alkyl or aryl halides, esters and carbon dioxide, and the reaction is said to proceed through the formation of an intermediate complex of the nature of a pseudohalogen (Kleinberg, *Chem. Rev.*, 1947, **40**, 381; Hunsdiecker *et al.*, *Chem. Abstracts*, 1940, **34**, 1685).  $\alpha$ -Bromo-esters have been prepared by the action of bromine on potassium salts of half-esters of dicarboxylic acids (Dice and Bowden, *J. Amer. Chem. Soc.*, 1949, **71**, 3107). But in all such cases, which are attended with simultaneous substitution and decarboxylation, the reactions are quite complex and can hardly be represented by any simple mechanism.

In the present case, we have definitely established the bimolecular nature of the reaction, which clearly points out that sodium acetate is the active reactant, undergoing direct bromine substitution. In a medium of such low dielectric constant as acetic acid, sodium acetate is only incompletely dissociated and exists as ion-pairs, most probably solvated (Kolthoff and Wilman, *J. Amer. Chem. Soc.*, 1934, **56**, 1007). The

reactivity of the acetate towards bromine, as against the relative inactivity of free acetic acid, can be explained by a mechanism involving sodium acetate ion-pairs and polarised bromine molecule (cf. Das and Palit, *loc. cit.*). The failure of the reaction in aqueous medium clearly suggests that acetic acid molecules have also got something to do in the matter, probably by way of solvation. In substitution reactions, bromine behaves as an electrophilic reagent and the reaction is facilitated by a high electron density at the point of attack. In the acetate ion, there is a concentration of negative charge on the  $\alpha$ -carbon atom due to the influence of the negatively charged oxygen, and this leads to substitution. The reaction possibly occurs through the formation of an activated complex of the type shown below :



It must be distinctly understood, however, that in the mechanism suggested above, bromine is supposed to act *not* through the formation of any free  $\text{Br}^+$  cation, but merely as an inductively *polarised* molecule. Free bromine cation is known to exist, in appreciable concentration, only in an aqueous solution of  $\text{HOBr}$  in presence of mineral acids (Derbyshire and Waters, *Nature*, 1949, **164**, 447 ; Weiss, *Ann. Reports*, 1947, **44**, 79). In most of the reactions with bromine, however, a mechanism involving free  $\text{Br}^+$  cation is inadmissible, as that would imply a specific reaction rate in excess of the collision frequency of this ion with the substance undergoing bromination (Bartlett and Tarbell, *J. Amer. Chem. Soc.*, 1936, **58**, 466).

DEPARTMENT OF PHYSICAL CHEMISTRY,  
INDIAN ASSOCIATION FOR THE CULTIVATION OF  
SCIENCE, CALCUTTA.

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SELECTIVE METHYLATION OF QUINACETOPHENONE. A NEW  
METHOD OF PREPARATION OF QUINACETOPHENONE  
MONOMETHYL AND DIMETHYL ETHERS

BY G. N. VYAS AND N. M. SHAH

In connection with other investigations, quinacetophenone monomethyl ether was required in large quantity. The method of Kostanecki and Lampe (*Ber.*, 1904, 37, 773) was found to be unsatisfactory as it led to the formation of a mixture of the mono- and dimethyl ethers, the yield of the monomethyl ether being considerably low. Kauffmann and Beisswenger (*Ber.*, 1905, 38, 789) obtained the monomethyl ether of quinacetophenone as a by-product in the Friedel-Crafts acetylation of quinol dimethyl ether. Baker (*J. Chem. Soc.*, 1939, 1922) prepared it by partial demethylation of quinacetophenone dimethyl ether. The above methods are not suitable for large-scale preparation and hence the present work was undertaken. The direct introduction of the acetyl group into the monomethyl ether of quinol was unsuccessfully tried by the Nencki as well as Hösch reactions, the unchanged monomethyl ether being recovered. Its Friedel-Crafts acetylation gave quinacetophenone in good yield, the demethylation occurring during the reaction. Similarly the Fries migration of its acetate resulted in the formation of quinacetophenone.

After several trials, it was found that the methylation of quinacetophenone by means of methyl iodide in acetone solution in presence of dry potassium carbonate could be satisfactorily effected, a good yield of its monomethyl ether being obtained (72%), without the contamination of the corresponding dimethyl ether.

*Quinacetophenone Dimethyl Ether.*—Quinacetophenone dimethyl ether has been prepared by various authors (Klages, *Ber.*, 1904, 37, 3996; Kauffmann and Bleiswenger, *loc. cit.*; Kuroda and Matsukuma, *British Chem. Abs.*, 1932, 388) by Friedel-Crafts acetylation of quinol dimethyl ether.

A direct methylation of quinacetophenone by dimethyl sulphate has now been investigated and after several trials, a satisfactory method of preparing the quinacetophenone dimethyl ether in quantity (70-75%) has been evolved.

The results indicate that quinacetophenone can be methylated either to get exclusively its monomethyl ether or dimethyl ether according to the methylating reagent used. The advantage of the methods described here consists in getting the mono or dimethyl ether as required directly from quinacetophenone without the contamination of the other product.

*Quinacetophenone Monomethyl Ether.*—Quinacetophenone (30 g., 1 mol.) was dissolved in hot acetone (300 c.c., 10 parts) and to the cooled solution, anhydrous potassium carbonate (28 g., 1 mol.) and methyl iodide (40 g., 1.5 mols.) were added. The mixture was then refluxed on a water-bath (60°-70°) for 5 to 6 hours. Most of the acetone was then recovered by distillation. The thick residual liquid after acidifying

with dilute sulphuric acid was subjected to steam distillation. The milky distillate on cooling gave pale greenish yellow, long needles; they were collected and crystallised from hot water, m. p.  $52-53^{\circ}$ , yield, 18-20 g., 80% calculated on the amount of quinacetophenone utilised. It is easily soluble in common organic solvents.

The residue in the flask after steam-distillation was filtered hot. On cooling, the brown needles separated, m. p.  $203^{\circ}$ , identified as quinacetophenone (7 g.), which can be re-used for methylation.

*Quinacetophenone Dimethyl Ether.*—To a boiling solution of quinacetophenone (60 g., 1 mol.) in alcohol (300 to 360 c.c., 5-6 parts), dimethyl sulphate (120 g., 2.4 g. mols.) and hot sodium hydroxide solution (40 g. in 100 c.c. water) were alternately added in small instalments and the mixture well stirred. It took nearly half an hour. The reaction mixture was strongly alkaline throughout. It was then refluxed on a water-bath for two hours. Alcohol was then removed and the residue subjected to steam-distillation. The distillate was extracted with ether after adding salt to it. A thick oil was obtained after removing ether. It was dried over anhydrous  $\text{CaCl}_2$  and distilled under reduced pressure, b. p.  $156^{\circ}-158^{\circ}/15$  mm. yield, 50.52 g. (70-75%). The purified distillate solidifies on cooling in ice bath.

M. R. SCIENCE INSTITUTE,  
GUJARAT COLLEGE,  
AHMEDABAD.

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# CHEMISTRY OF THE RARE EARTHS. PART VII. DISSOCIATION CONSTANTS OF THE THIOSULPHATES OF RARE EARTHS

BY NIHAR KUMAR DUTT

Dissociation constants of the thiosulphates of rare earths (La, Ce, Pr, Nd and Sm) have been measured. These values have been found to follow the "Serial Order" of the rare earths.

In a previous communication (Part VI, this *Journal*, 1949, 26, 405), the composition and isolation of several double thiosulphates of rare earths have been described. It has been shown there that the reactions between different alkali thiosulphates and rare earth salts take place in two steps, at first the simple thiosulphates  $R_2(S_2O_3)_3$  are formed by the following reaction,



and next double thiosulphates are formed having compositions  $[R(S_2O_3)_4]^{4-}$  and  $[R(S_2O_3)_5]^{5-}$  with sodium and potassium (also ammonium) thiosulphates respectively where R stands for La, Ce, Pr, Nd and Sm. The determination of dissociation constants of the simple thiosulphates forms the subject matter of the present communication.

## EXPERIMENTAL

Dissociation constants have been determined by the method of continued variation of Job (*Compt. rend.*, 1928, 180, 928). The general principle of this method and the actual experimental procedure for the application of the same in this particular case have been described in Part VI of this series (*loc. cit.*).

In this method, Job has shown that the maximum composition "x" does not change when the concentrations of the two primary solutions used, are equimolecular. By maximum composition is meant the composition corresponding to the formation of the maximum amount of the compound in question. In other cases, that is, in cases where the concentrations are non-equimolecular, it varies and depends both upon the concentrations of two primary solutions and upon the equilibrium constant K for the reaction. Hence, the value of this maximum composition "x" determines with the help of the general equation of Job the equilibrium constant K.

For this purpose, the values of m and n, 2 and 3 respectively, as determined previously, are substituted in the general equation of Job,

$$K = \frac{C^{m+n-1} \times p^{n-1} \times \{(pm+n)x-n\}^{m+n}}{m^{n-1} \cdot n^{m-1} \cdot (p-1)^{m+n-1} \{n-(m+n)x\}} \quad \dots (2)$$

when we get;

$$K = \frac{C^4 \cdot p^2 [(2p+3)x-3]^5}{12(p-1)^4 (3-5x)} \quad \dots (3)$$



Series of measurements are then carried out in the lines as with equimolecular solutions and from the respective curves drawn, the values of  $x$ , i. e. positions of maxima on the curves, are determined and substituted in equation (3).

The results are represented graphically in Figs. 1-5.

The values of  $C$ , the initial molar concentrations of the rare earth salts, taking complete dissociation at these dilutions, where molar concentrations are equal to ionic concentrations,  $p = C'/C$ , where  $C'$  is the initial molar concentration of the thiosulphate solution, and  $x$  being known, the dissociation constants have been calculated with the help of the equation (3) and these are shown in Tables I-V.

TABLE I  
Dissociation constant of  $\text{La}_2(\text{S}_2\text{O}_3)_3$ .

Temp. =  $32^\circ \pm 0.05^\circ$ .

	$C$ .	$p$ .	$x$ .	$K$ .	Ref.
1	0.025	4	0.35	$1.28 \times 10^{-9}$	Fig. 1, curve I
2	0.01	10	0.27	$2.64 \times 10^{-9}$	Fig. 1, curve II
3	0.01	4	0.42	$2.04 \times 10^{-9}$	Fig. 1, curve III
4	0.01	2	0.535	$2.44 \times 10^{-9}$	Fig. 1, curve IV
				Mean $2.35 \times 10^{-9}$	

TABLE II  
Dissociation constant of  $\text{Ce}_2(\text{S}_2\text{O}_3)_3$ .

Temp. =  $32^\circ \pm 0.05^\circ$ .

	$C$ .	$p$ .	$x$ .	$K$ .	Ref.
1	0.025	4	0.32	$1.74 \times 10^{-10}$	Fig. 2, curve I
2	0.01	10	0.22	$2.48 \times 10^{-10}$	Fig. 2, curve II
3	0.01	4	0.37	$2.02 \times 10^{-10}$	Fig. 2, curve III
4	0.01	2	0.50	$2.08 \times 10^{-10}$	Fig. 2, curve IV
				Mean $2.08 \times 10^{-10}$	

TABLE III  
Dissociation constant of  $\text{Pr}_2(\text{S}_2\text{O}_3)_3$ .

Temp. =  $32^\circ \pm 0.05^\circ$ .

	$C$ .	$p$ .	$x$ .	$K$ .	Ref.
1	0.02	5	0.27	$2.72 \times 10^{-11}$	Fig. 3, curve I
2	0.01	4	0.34	$2.81 \times 10^{-11}$	Fig. 3, curve II
3	0.01	5	0.30	$3.21 \times 10^{-11}$	Fig. 3, curve III
4	0.01	2	0.48	$3.36 \times 10^{-11}$	Fig. 3, curve IV
				Mean $3.02 \times 10^{-11}$	

TABLE IV

Dissociation constant of  $\text{Nd}_2(\text{S}_2\text{O}_3)_3$ .Temp. =  $32^\circ \pm 0.05^\circ$ .

	C.	p.	$\alpha$ .	K.	Ref.
1	0.02	5	0.265	$1.36 \times 10^{-11}$	Fig. 4, curve I
2	0.01	4	0.33	$1.21 \times 10^{-11}$	Fig. 4, curve II
3	0.01	5	0.29	$1.42 \times 10^{-11}$	Fig. 4, curve III
4	0.01	2	0.47	$1.05 \times 10^{-11}$	Fig. 4, curve IV
				Mean $1.26 \times 10^{-11}$	

TABLE V

Dissociation constant of  $\text{Sm}_2(\text{S}_2\text{O}_3)_3$ .Temp. =  $32^\circ \pm 0.05^\circ$ .

	C.	p.	$\alpha$ .	K.	Ref.
1	0.01	4	0.32	$4.47 \times 10^{-12}$	Fig. 5, curve I
2	0.01	5	0.28	$5.46 \times 10^{-12}$	Fig. 5, curve II
3	0.01	6	0.25	$6.52 \times 10^{-12}$	Fig. 5, curve III
4	0.01	3	0.38	$5.56 \times 10^{-12}$	Fig. 5, curve IV
				Mean $5.50 \times 10^{-12}$	

FIG. 1

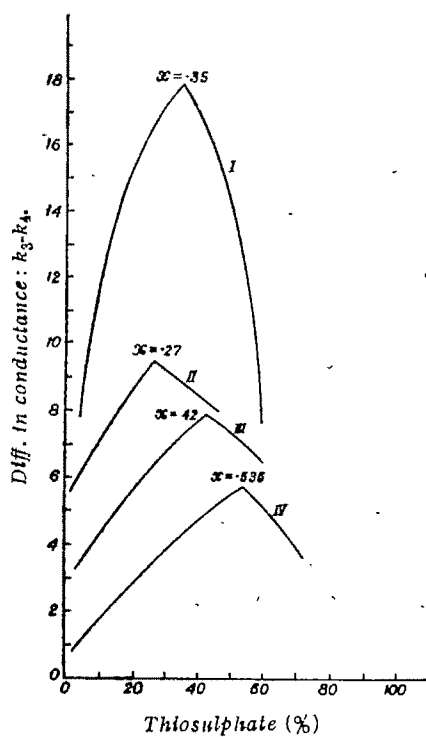


FIG. 2

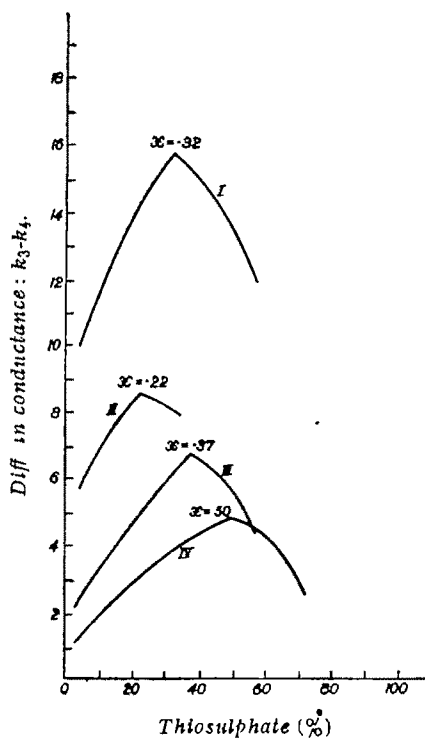


FIG. 3

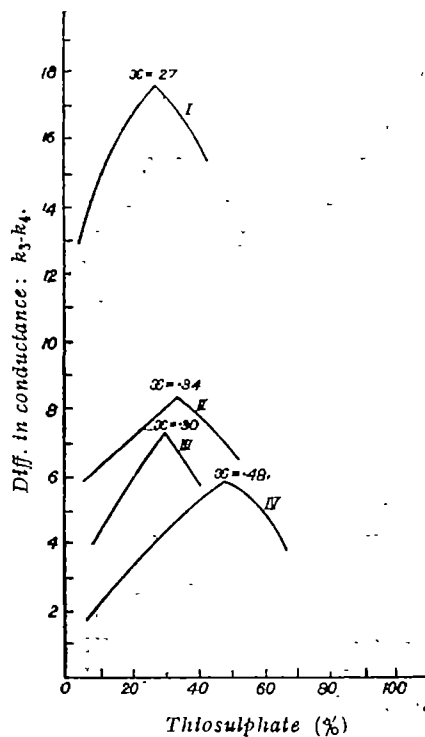


FIG. 4

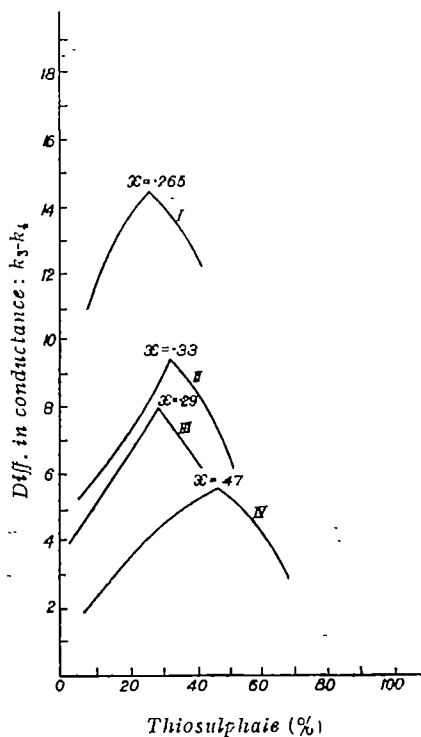
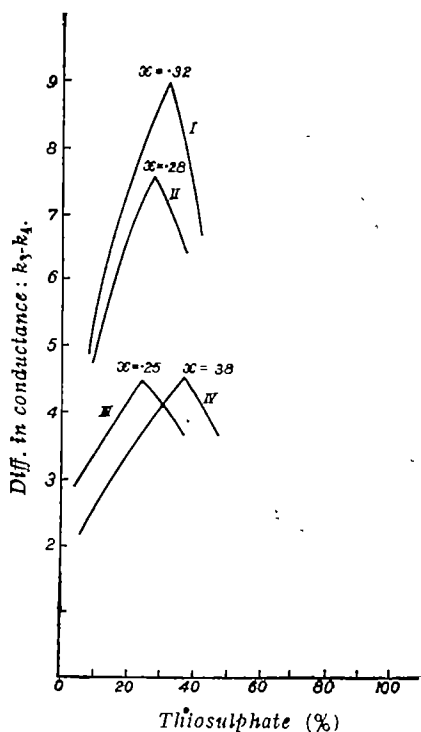


FIG. 5



All measurements have been made in an electrically regulated thermostat capable of keeping the temperature constant with  $\pm 0.05^\circ$ .

The values found for  $K$ , evidently shows that the stabilities of the salts follows the serial order of the rare earths as has been pointed out earlier.

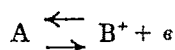
The author's thanks are due to Prof. P. B. Sarkar for his kind and helpful suggestions during the progress of the work.

## A METHOD FOR CALCULATING ABSOLUTE SINGLE ELECTRODE POTENTIAL

BY S. N. BAGCHI

A new method has been developed depending upon the maximum heat that could be done in passing from one state to the other or *vice versa*, for calculating absolute single electrode potential.

Every electrode process is an oxidation-reduction process, since it involves gain or loss of electrons by atoms or ions and can be represented by the equation,



Our problem is to find out the maximum work that could be done in passing from state A to state B<sup>+</sup> or *vice versa*. If this work is performed electrically, we get the desired e.m.f. Thus; when *n* electrons are involved,

$$enV = -\Delta F = kT \ln K = kT \ln [ne] + kT \ln \frac{[B^+]}{[A]}$$

$$\text{or} \quad V = \frac{kT}{ne} \ln [ne] + \frac{kT}{ne} \ln \frac{[B^+]}{[A]}$$

= *V*<sub>0</sub>, when the activities of B<sup>+</sup> and A are unity.

Here, *V*<sub>0</sub> = the standard absolute electrode potential,

*K* = the equilibrium constant,

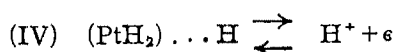
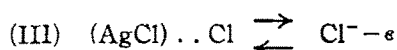
Δ*F* = the maximum work done upon the system i.e., the gain in free energy,

*e* = the electronic charge,

*n* = the number of electrons transferred, and

*V* = the absolute electrode potential.

Let us consider the following cases



*Case I.*—Here both  $\text{Fe}^{++}$  and  $\text{Fe}^{+++}$  ions are in solution and the process of transformation is simply the transference of one electron from  $\text{Fe}^{++}$ . Let the work, to be done on the system, to extract one electron from  $\text{Fe}^{++}$  be  ${}_2J_3$  electron volts. When there is a suitable indifferent electrode in the medium, e. g., Pt, this work is converted into electrical work by the passage of the liberated electron which therefore gives an e. m. f. equal to  ${}_2J_3$  volts. The work is done upon the system by the oxidising agent and the electrode here acts only as a channel for the passage of electrons. The e. m. f. therefore ought not to depend on the nature of the electrode provided that no chemical reaction takes place between the electrode and the medium.

Table I, taken from Gurney ('Ions in Solution', Cambridge University Press, 1936, pp. 117-178), give the ' ${}_mJ_m$ ' values for several such red-ox systems, as well as their standard potentials referred to the hydrogen electrode. Since  ${}_mJ_m$  is the absolute potential of the system, we easily get the absolute potential of the hydrogen electrode from their relative values. It will be noted that the difference of  $J$  values is the same as that in the relative scale.

TABLE I

System.	' ${}_mJ_m$ ' electron.	Standard red-ox potentials in aq. soln. referred to the H-electrode.	Absolute potential of the H-electrode.
$\text{Cr}^{++} \rightleftharpoons \text{Cr}^{+++}$	3.67 volts	-0.4 volt	4.07 volts
$\text{Ti}^{++} \rightleftharpoons \text{Ti}^{+++}$	4.4	+0.37	4.03
$\text{Fe}^{++} \rightleftharpoons \text{Fe}^{+++}$	4.8	+0.75	4.05
$\text{Ce}^{+++} \rightleftharpoons \text{Ce}^{++++}$	5.6	+1.55	4.05
$\text{Co}^{++} \rightleftharpoons \text{Co}^{+++}$	5.9	+1.82	4.08

*Case II.*—The reaction is equivalent to the transference of a silver atom (i.e.  $\text{Ag}^+$  ion core *plus* an electron) from the metallic lattice to the solution in the ionic form. The energy difference between the two states can be calculated by considering the following mechanism. First the silver atom is evaporated from the lattice which would require the energy of sublimation,  $S$ . The vaporised atom is then ionised and finally solvated. The total energy required is  $S+I-W$ , where  $I$  and  $W$  are ionisation and solvation energies. When all of them are expressed in electron volts, the absolute standard electrode potential of the system is given by\*,

$$V_0 = S + I - W.$$

Gurney (*ibid.*, Chap. XIV, p. 202) has given the values of heat of solvation for various ions as well as the relation between the heat of solvation and solvation energies. Table II gives the absolute potential of the hydrogen electrode calculated from this picture.

\* As the entropies of  $\text{Ag}^+$  ions in the metallic lattice and in the solution are different, the whole of this amount of energy could not be converted into useful work. The potential, in that case, would be given by Gibbs—Helmholtz relation.

TABLE II

System.		Absolute values of e.m.f. ( $S+I-W$ ).	Standard electrode potential referred to H-electrode.	Absolute pot. of the H-electrode
Ag	$\begin{array}{c} \rightarrow \\ \leftarrow \end{array}$	Ag <sup>+</sup> (2.90+7.54-5.5)=4.94 volts	+0.798 volt	4.142 volts
K	$\begin{array}{c} \rightarrow \\ \leftarrow \end{array}$	K <sup>+</sup> (0.94+4.32-4.1)=1.16	-2.924	4.084
Rb	$\begin{array}{c} \rightarrow \\ \leftarrow \end{array}$	Rb <sup>+</sup> (0.87+4.16-3.8)=1.23	-2.926	4.156

Case III.—The process consists in tearing away a chlorine atom from the AgCl lattice, dissociating the resulting chlorine molecule, ionising a chlorine atom and finally passing the anion into solution. If  $Q$  be the heat of formation† of AgCl from Ag and Cl<sub>2</sub> molecules;  $D$ , the dissociation energy of Cl<sub>2</sub> molecules;  $I$ , the electron affinity of the chlorine atom;  $W$ , the solvation energy of the Cl<sup>-</sup> ion, then the energy gained is

$$\frac{1}{2}Q + \frac{1}{2}D - I - W = (1.20 + 1.23 - 3.8 - 2.8) \text{ e.v.} = -4.17 \text{ e.v.}$$

Since here the anion is transferred, the absolute potential of the electrode is +4.17 volts. Standard potential of AgCl-Cl<sup>-</sup> electrode is +0.22 volt. Hence, the absolute potential of the hydrogen electrode is +3.97 volts.

Case IV.—Here the equilibrium is between the hydrogen atom and the hydrogen ion in the solution. Hence the energy required to take one hydrogen atom from the gaseous state to the solution in the ionic form is

$$(\frac{1}{2}D + I - W) = (2.24 + 13.53 - 12.0) = 3.77 \text{ e.v.}$$

where  $D$  is the dissociation energy and  $I$ , the ionisation energy. Now, if we add to this the energy of desorption of hydrogen molecules from the surface of the platinum black, about 0.35 electron volt per atom of hydrogen\*, we get the value of absolute potential of the hydrogen electrode as 4.12 volts.

The kinetic picture would be the same as that visualised by Gurney (*loc. cit.*, pp. 85-88). When a metal is dipped into the solution containing its ions, either the metal ions will go into solution or the ions in the solution will be deposited on the surface of the lattice depending on their relative energies of solution and deposition until a potential  $V$  is set up on the surface of the metal which prevents further solution or deposition. In other words, at the equilibrium stage, the number of ions passing into solution must be equal to the number of ions deposited.

† I have again assumed that this energy is converted not into heat but into useful work. Otherwise, the energy difference between any two states and the difference in their free energies would, in all cases, be related by Gibbs-Helmholtz equation and taking the experimentally determined values of  $dV/dT$  we could easily calculate the value of  $V$ .

\* The heat of desorption of molecular hydrogen is known only approximately and as given by Glasstone ("Recent Advances in Physical Chemistry", J.A. Churchill Ltd., 1936, p.428) it lies between -10,000 and -25,000 cal. per mole.

Now, the fraction of the total number of ions on the surface of the lattice having energies greater than  $U_m - nev$  is given by  $\int_0^\alpha e^{-\frac{U-U_m+nev}{kT}} dU$  where  $U_m$  is the minimum energy required to take an ion out of the lattice. For the ions in solution the number is given by  $\int_0^\alpha e^{-\frac{U-W}{kT}} dU$ . The probability of a metallic ion going into solution will depend on the number of solvent molecules  $N_s$  and that of ions in solution to deposit, on the number of solute particles  $N$ . Hence at equilibrium

$$N_s \int_0^\alpha e^{-\frac{U-U_m+nev}{kT}} dU = N \int_0^\alpha e^{-\frac{U-W}{kT}} dU$$

or,  $V = + \frac{U_m - W}{ne} + \frac{kT}{ne} \ln C$  where  $C = N/N_s$

or  $V = V_0 + \frac{kT}{ne} \ln a,$

if we substitute the concentration by the activity which depends on the effective number of solute molecules colliding on the surface of the metal.

Considering the widely different mechanisms employed and the fact that none too accurate values of relevant data are available the agreement between the different cases seems striking. In case I both the components ( $\text{Fe}^{++}$  and  $\text{Fe}^{+++}$ ) are in the same phase and the maximum work obtained here gives directly the changes in free energy. The most probable value of the absolute potential of the hydrogen electrode would therefore be in the neighbourhood of 4.05 volts.

# A NEW EQUATION FOR STRONG ELECTROLYTES. PART I

By S. N. BAGCHI

An equation for uni-univalent strong electrolytes has been derived.

Assuming the concept of ion atmosphere and the validity of Poisson's equation as put forward by Debye and Hückel (*Physikal. Z.*, 1923, 24, 185) an equation, which has been found to be valid in a few test cases up to 4*N*, has been derived for uni-univalent strong electrolytes. The equation has been derived on the basis of two hypotheses :

(1) The total number of particles, i.e. the sum of the positive and negative ions, per unit volume remains constant.

(2) The number of positive and negative ions per unit volume around a central ion would then be given not by Boltzmann's distribution\* but by a distribution of the type

$$n_+ = \frac{\sum_i n_i}{e^{\epsilon\psi/kT} + 1} \quad \dots \quad (1)$$

$$n_- = \frac{\sum_i n_i}{e^{-\epsilon\psi/kT} + 1}$$

where  $\sum_i n_i$  is the total number of particles, i.e. sum of all the ions present, per unit volume ;

$n_+$  and  $n_-$  are the numbers of positive and negative ions per unit volume ;

$\epsilon$  is the electronic charge ;

$k$  is the Boltzmann's constant ;

$T$  is the absolute temperature ;

$\psi$  is the potential at any point due to all the ions present with respect to a particular central ion.

\* The condition that the total number of ions per unit volume should remain the same could be arrived at from a modified Boltzmann's distribution of the type,

$$n_+ = Ae^{-\epsilon\psi/kT} \quad \text{and} \quad n_- = Ae^{\psi/kT} \quad \dots \quad (1a)$$

$$\text{where } A = \frac{\sum_i n_i}{e^{-\epsilon\psi/kT} + e^{\psi/kT}} \quad \dots \quad (1b)$$

Poisson's equation would then assume the form

$$\nabla^2 \lambda = K^2 \tan h \lambda$$

$$\text{where } \lambda = \epsilon\psi/kT \quad \text{and} \quad K^2 = \frac{4\pi\epsilon^2 \sum_i n_i}{DkT}$$

But the author has found that the values of activity coefficients of electrolytes calculated by using this formula do not agree with those obtained experimentally.



The charge density

$$\begin{aligned}\rho &= (n_+ - n_-)e \\ &= -\sum_i n_i e \tanh h \frac{e\psi}{2kT}\end{aligned}\quad \dots (2)$$

It will be seen that  $\rho$  remains finite even when  $\psi \rightarrow \infty$

Poisson's equation would then assume the form

$$\nabla^2 \psi = \frac{4\pi \sum_i n_i e}{D} \tanh h \frac{e\psi}{2kT} \quad \dots (3)$$

$$\text{or} \quad \nabla^2 \lambda = K^2 \tanh \lambda \quad \dots (4)$$

where,  $D =$  the dielectric constant of the medium

$$\begin{aligned}\lambda &= \frac{e\psi}{2kT} \\ K^2 &= \frac{2\pi e^2 \sum_i n_i}{DkT}\end{aligned}\quad \dots (5)$$

In order to solve the equation (4) it has been separated into two parts

$$\nabla^2 \lambda = K^2 \lambda \text{ for small values of } \lambda \quad \dots (6)$$

$$\text{and} \quad \nabla^2 \lambda = K^2 \quad \text{for large values of } \lambda \quad \dots (7)$$

$$\text{or} \quad \frac{1}{\xi^2} \cdot \frac{d}{d\xi} \left( \xi^2 \frac{d\lambda}{d\xi} \right) = \lambda \quad \dots (6a)$$

$$\text{and} \quad \frac{1}{\xi^2} \cdot \frac{d}{d\xi} \left( \xi^2 \frac{d\lambda}{d\xi} \right) = 1 \quad \dots (7a)$$

$$\text{where } \xi = Kr$$

With the boundary condition that  $\lambda$  tends to 0 as  $\xi \rightarrow \infty$  Eqn (6a) gives

$$\lambda = \frac{Be^{-\xi}}{\xi} \quad \dots (8)$$

and solving Eqn. (7a) we get

$$\lambda = \frac{\xi^2}{6} + c + \frac{H}{\xi} \quad \dots (9)$$

where  $B$ ,  $C$  and  $H$  are constants of integration to be determined.

In order to find out  $C$  and  $H$ , the two curves given by the equation (8) and (9) are fitted at the point  $\xi_1$  where  $\lambda$  is equal to 1, for if at this point  $\lambda_1 = \lambda_2$

$$\text{and} \quad \frac{d\lambda_1}{d\xi} = \frac{d\lambda_2}{d\xi} \quad \text{then} \quad \frac{d^2\lambda_1}{d\xi^2} \quad \text{would be equal to} \quad \frac{d^2\lambda_2}{d\xi^2}$$

where  $\lambda_1$  and  $\lambda_2$  are the values of  $\lambda$  for the equations (8) and (9) respectively.

Thus we get

$$H = \frac{\xi_1^3}{3} + \xi_1^2 + \xi_1 \quad \dots (10)$$

$$C = \frac{1}{2} \left[ 1 - (\xi_1 + 1)^2 \right] \quad \dots (11)$$

Now, in order to find out  $H$  and therefore  $\xi_1$  and  $C$  we assume the continuity of normal induction on the surface of the ion. It is obvious that Eqn. (8) is valid in the neighbourhood of infinity and Eqn. (9) in the neighbourhood of zero. Hence using Eqn. (9) we get

$$H = \frac{\epsilon^2 K}{2DkT} + \frac{K^3 a_i^3}{3} \quad \dots (12)$$

where  $a_i$  is the effective ionic radius of the central ion.

Thus

$$\begin{aligned} \xi_1 &= (1 + 3H)^{1/3} - 1 \\ &= \left( 1 + \frac{3\epsilon^2 K}{2DkT} + K^3 a_i^3 \right)^{1/3} - 1 \quad \dots (12a) \end{aligned}$$

$$= (1 + g)^{1/3} - 1 \quad \dots (12b)$$

$$\text{where } g = \frac{3\epsilon^2 K}{2DkT} + K^3 a_i^3 \quad \dots (12c)$$

$$\text{and } C = \frac{1}{2} \left[ 1 - (1 + g)^{2/3} \right] \quad \dots (13)$$

Hence  $\psi_0$ , the potential due to the ion atmosphere on the surface of the central ion is given by

$$\begin{aligned} \psi_0 &= \psi_{a_i} - \frac{e}{Da_i} \\ &= \frac{kT}{e} \cdot K^2 a_i^2 + \frac{kT}{e} \left[ 1 - (1 + g)^{2/3} \right] \quad \dots (14) \end{aligned}$$

Now, following Debye (*Physikal. Z.*, 1924, 25, 97) we can calculate the maximum work due to electrostatic forces (short range interactions, e.g. forces of polarisation, etc., have been neglected) which would give the difference between the thermodynamic potential of the real solution and the ideal solution

$$\begin{aligned} \text{This work } W &= \int_0^1 \epsilon \psi_{0x} dx \\ &= kT \cdot K^2 a_i^2 \int_0^1 x dx + kT \int_0^1 \frac{1 - (1 + gx^3)^{2/3}}{x} dx \\ &= \frac{1}{2} kTK^2 a_i^2 + kTP + kT\phi(g) \quad \dots (15) \end{aligned}$$

$$\text{where } P = \frac{1}{2} + \frac{1}{\sqrt{3}} \tan^{-1} \sqrt{3} - \frac{1}{2} \ln 3$$

$$\begin{aligned} \phi(g) = \frac{1}{2} \ln \left\{ (1+g)^{2/3} + (1+g)^{1/3} + 1 \right\} \\ - \frac{1}{\sqrt{3}} \tan^{-1} \frac{2(1+g)^{1/3} + 1}{\sqrt{3}} - \frac{1}{2} (1+g)^{2/3} \quad \dots (15a) \end{aligned}$$

$$\text{Hence the total work } \bar{W} = \sum_i n_i W_i \quad \dots (16)$$

and the activity coefficient  $f_i$  of the ion, by definition, is given by the equation

$$\begin{aligned} \ln f_i &= \frac{1}{kT} \frac{\delta \bar{W}}{\delta n_i} \\ &= K^2 a_i^2 + P + \phi(g) + \sum_i n_i \frac{\delta \phi}{\delta n_i} \quad \dots (17) \end{aligned}$$

$$\begin{aligned} \text{where } \dots \quad \sum_i n_i \frac{\delta \phi}{\delta n_i} &= \frac{1}{2} \left[ \frac{\frac{\epsilon^2 K}{2DkT} + K^2 a_i^2}{(1+g)^{1/3}} + \frac{\frac{\epsilon^2 K}{2DkT} + K^2 a_i^2}{2(1+g)^{2/3}} \right. \\ &\quad \left. - \frac{\epsilon^2 K / 2DkT + K^2 a_i^2}{3(1+g)^{2/3} \{1 + \frac{1}{3} [2(1+g)^{1/3} + 1]^2\}} - \frac{1}{2} \frac{\epsilon^2 K / 2DkT + K^2 a_i^2}{(1+g)^{1/3}} \right] \quad (17a) \end{aligned}$$

The mean activity coefficient of the electrolyte is therefore given by

$$\ln f_{\pm} = \frac{\ln f_+ + \ln f_-}{2} \quad \dots (18)$$

Table I gives the mean activity coefficients of CsCl and KCl in the *molar scale of concentration* (*g. moles per litre of solution*) calculated from the formulae (17 and 18) and using the following ionic radii,  $\text{Cs}^+ = 1.67 \text{ \AA}$ ,  $\text{K}^+ = 1.33 \text{ \AA}$  and  $\text{Cl}^- = 1.81 \text{ \AA}$ , as given by crystallographic data and the dielectric constant of water.

TABLE I

Mean activity coefficients at 25°.

	0.01N.	1.0N.	4.0N.
CsCl	0.9239	0.5702	0.4466
KCl	0.9237	0.5581	0.4163
		0.6209*	0.5667*

\* The values are for KCl when the ionic radius of  $\text{K}^+$  is taken as 2.76 Å.

Table II gives the observed data of mean activity coefficients at 25° in *molal scale of concentration* (*g. moles per 1000 g. of solvent*). The values for molar scale would be slightly less.

TABLE II

*Mean activity coefficients  $f_{\pm}$  at 25° in molal scale of concentration.*

	0.01M.	1.0M.	4.0M.
KCl	0.922†	0.634†	0.582‡
		0.605‡	
CsCl		0.543‡	0.474‡

† Falkenhagen, "Electrolytes," Oxford University Press, 1939, pp. 65, 67.

‡ Harned &amp; Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold Publishing Corp., 1943, p. 562.

It will be seen that for CsCl the calculated values given in Table I agree well with the observed data. The low values for KCl at higher concentrations are due to the hydration of  $K^+$  ions. If we consider the  $K^+$  ion packed within a layer of water molecules of diameter 2.76 Å and use 2.76 Å as the effective ionic radius for the  $K^+$  ion, the values for the activity coefficients of KCl for 1N and 4N become respectively 0.6209 and 0.5667 which show satisfactory agreement with the observed values.

The equation also explains how at higher concentrations the activity coefficients may become greater than unity.

It will be noted that here the ions have been assumed to be spherically symmetrical. The equation (17) therefore will not be valid for spherically unsymmetrical ions like  $NO_3^-$ ,  $SO_4^{2-}$  or for rod shaped particles of long chain compounds and colloidal electrolytes.

UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,  
CALCUTTA,

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# A NEW EQUATION FOR STRONG ELECTROLYTES. PART II

BY S. N. BAGCHI

The new equation for uni-univalent strong electrolytes has been generalised for any binary electrolyte.

In a previous communication (this *issue*, p. 199), an equation has been derived for univalent strong electrolyte. In this paper the equation has been generalised for any binary electrolyte,  $X_\mu Y_\nu$ . Moreover, the restriction imposed therein under assumption (1) has been removed. The number of positive and negative ions per unit volume around a central ion is given not by Boltzmann's distribution but by an analogous Fermi-Dirac distribution (cf. Dutta and Bagchi, *Indian J. Phys.*, 1950, 24, 16) wherein the proportionality constant is taken to be equal to the total number of ions present, since the potential in any solution of the electrolyte presumably depends on all the ions present.

The distribution is then given by

$$\left. \begin{aligned} n_+ &= \frac{N}{A_+ e^{z_+ \lambda} + 1} \\ n_- &= \frac{N}{A_- e^{z_- \lambda} + 1} \end{aligned} \right\} \dots (1)$$

where  $N$  is the total number of ions present per unit volume and  $n_+$  and  $n_-$  are the number of positive and negative ions per unit volume.

$Z_+$  and  $Z_-$  are the valencies of positive and negative ions;  $A_+$  and  $A_-$  are the constants to be determined.  $\lambda = e\psi/kT$ ;  $\psi$  = the potential at any point around a central ion;  $e$ ,  $k$ ,  $T$  have their usual significances.

Consider a central positive ion of valency  $Z_+$  at a concentration (molar)  $C$  of the electrolyte  $X_\mu Y_\nu$ . At a distance where there is no field *i.e.*, where  $\psi \rightarrow 0$ , the number of positive ions is  $\mu C$  and that of negative ions is  $\nu C$

$$\left. \begin{aligned} \text{Hence } n_+ &= \frac{(\mu + \nu) C}{A_+ + 1} = \mu C \\ \text{or } A_+ &= \frac{\nu}{\mu} = \frac{Z_-}{Z_+} \\ \text{Similarly, } A_- &= \frac{Z_-}{Z_+} \end{aligned} \right\} \dots (2)$$

Therefore the charge density

$$\begin{aligned} \rho &= Ne \left[ \frac{Z_+}{\frac{Z_+}{Z_-} e^{z_+ \lambda} + 1} - \frac{Z_-}{\frac{Z_-}{Z_+} e^{-z_- \lambda} + 1} \right] \\ &= Ne Z_+ Z_- \left[ \frac{1}{Z_+ e^{z_+ \lambda} + 1} - \frac{1}{Z_- e^{-z_- \lambda} + 1} \right] \end{aligned}$$

Now for  $\lambda \rightarrow 0$

$$\rho \approx -N\epsilon Z_+ Z_- \frac{(Z_+^2 + Z_-^2)}{(Z_+ + Z_-)^2} \lambda$$

and for  $\lambda \rightarrow \infty$

$$\rho \approx -N\epsilon Z_-$$

Hence Poisson's equation gives

$$\nabla^2 \psi = -\frac{4\pi}{D} \rho$$

which for  $\lambda \rightarrow 0$  reduces to

$$\nabla^2 \lambda = \frac{4\pi N\epsilon^2 Z_+ Z_- (Z_+^2 + Z_-^2)}{DkT(Z_+ + Z_-)^2} \lambda = K^2 \lambda \quad \dots \text{ (II)}$$

and for  $\lambda \rightarrow \infty$  to

$$\begin{aligned} \nabla^2 \lambda &= \frac{4\pi N\epsilon^2 Z_-}{DkT} \\ &= \frac{4\pi N\epsilon^2 Z_+ Z_- (Z_+^2 + Z_-^2)}{DkT(Z_+ + Z_-)^2} \cdot \frac{(Z_+ + Z_-)^2}{Z_+ (Z_+^2 + Z_-^2)} \\ &= K^2 m_+ \end{aligned} \quad \dots \text{ (III)}$$

$$\left. \begin{aligned} K^2 &= \frac{4\pi N\epsilon^2 Z_+ Z_- (Z_+^2 + Z_-^2)}{DkT(Z_+ + Z_-)^2} \\ m_+ &= \frac{(Z_+ + Z_-)^2}{Z_+ (Z_+^2 + Z_-^2)} \end{aligned} \right\} \quad \dots \text{ (3)}$$

Now, proceeding as before and fitting the curves of the two equations (II) and (III) at  $\lambda = m_+$  we get finally

$$\ln f_+ = \frac{m_+}{2} \left[ K^2 a_+^3 + P + \phi(g) + \sum_i n_i \frac{\partial \phi}{\partial n_i} \right] \quad \dots \text{ (4)}$$

where  $a_+$  is the effective ionic radius of the central ion

$$\left. \begin{aligned} P &= \frac{1}{2} + \frac{1}{\sqrt{3}} \tan^{-1} \sqrt{3} - \frac{1}{2} \ln 3 \\ \phi(g) &= \frac{1}{2} \ln \{ (1+g)^{2/3} + (1+g)^{1/3} + 1 \} - \frac{1}{\sqrt{3}} \tan^{-1} \frac{2(1+g)^{1/3} + 1}{\sqrt{3}} - \frac{1}{2} (1+g)^{2/3} \\ \sum_i n_i \frac{\partial \phi}{\partial n_i} &= \frac{1}{2} \frac{h}{(1+g)^{2/3} + (1+g)^{1/3} + 1} + \frac{h}{2(1+g)^{2/3}} - \frac{h}{3(1+g)^{2/3} \{ 1 + \frac{1}{3} [2(1+g)^{1/3} + 1]^2 \}} - \frac{h}{2(1+g)^{2/3}} \\ h &= \frac{Z_+ \epsilon^2 K}{m_+ DkT} + K^3 a_+^3 \\ g &= \frac{3Z_+ \epsilon^2 K}{m_+ DkT} + K^3 a_+^3 \end{aligned} \right\} \quad (4a)$$

Hence the mean activity coefficient,  $f_{\pm}$ , of the electrolyte is given by

$$\ln f_{\pm} = \frac{Z_- \ln f_+ + Z_+ \ln f_-}{Z_+ + Z_-} \quad \dots (5)$$

It will be noted that all the above equations are reduced to the corresponding equations for uni-univalent electrolytes given in the previous communication.

FIG. 1

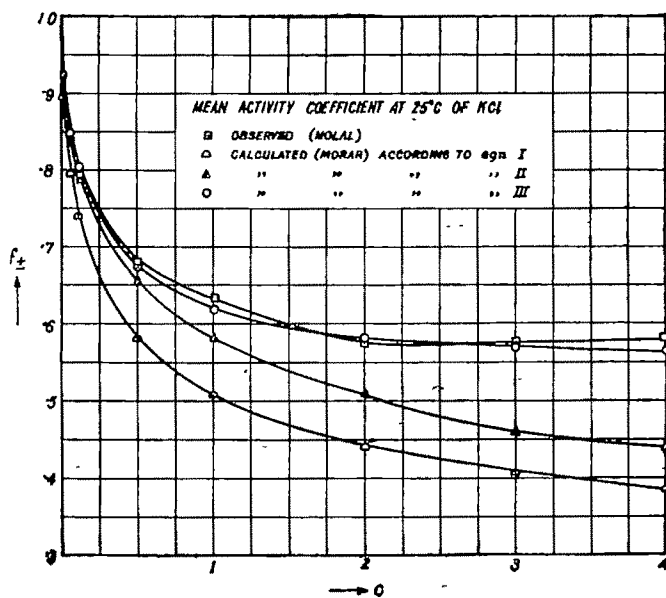
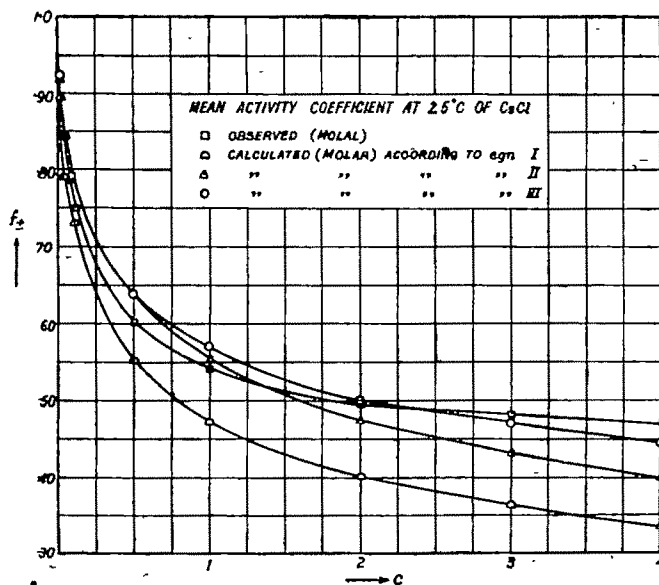


FIG. 2



Tables I, II and Figs. 1 and 2 give the observed (in the molal scale of concentration) and calculated (in the molar scale of concentration) values of activity coefficient of KCl and CsCl. The columns I, II and III refer to the values of activity coefficients calculated respectively from Debye's equation  $\nabla^2\lambda = K^2\lambda$  (I)

where  $K^2 = \frac{4\pi e^2}{DkT} \sum_i n_i Z_i^2$  and from equations

$\nabla^2\lambda = K^2\lambda$  (II) and  $\nabla^2\lambda = K^2m_+$  (III)

where  $K_2 = \frac{4\pi N e^2 Z_+ Z_- (Z_+^2 + Z_-^2)}{DkT(Z_+ + Z_-)^2}$  and  $m_+ = \frac{(Z_+ + Z_-)^2}{(Z_+^2 + Z_-^2)Z_+}$  ... (3)

TABLE I

Mean activity coefficients of KCl at 25°.

Conc.	Observed (molal).	Calculated (molar) ( $a_+ = 2.76\text{\AA}$ , $a_- = 1.81\text{\AA}$ )		
		I	II	III
0.01	0.922*	0.8966	0.9243	0.9253
0.05	0.840*	0.7987	0.8472	0.8502
0.1	0.794*, 0.769	0.7408	0.7987	0.8046
0.5	0.682*, 0.650	0.5802	0.6521	0.6759
1	0.634*, 0.605	0.5091	0.5794	0.6222
2	0.575	0.4433	0.5091	0.5820
3	0.573	0.4087	0.4698	0.5701
4	0.582	0.3860	0.4433	0.5666

\* Falkenhagen, "Electrolytes" (1934). All other values have been taken from Harned and Owen, "The Physical Chemistry of Electrolytic Solutions", (1943).

TABLE II

Mean activity coefficient of CsCl at 25°.

Conc.	Observed (molal)	Calculated ( $a_+ = 1.67\text{\AA}$ )		
		I	II	III
0.01	—	0.8950	0.9234	0.9241
0.05	—	0.7927	0.8435	0.8453
0.1	0.755	0.7307	0.7927	0.7956
0.5	0.664	0.5542	0.6339	0.6409
1	0.543	0.4742	0.5542	0.5669
2	0.495	0.3997	0.4742	0.5010
3	0.480	0.3603	0.4297	0.4671
4	0.474	0.3347	0.3996	0.4462



It will be seen that the agreement with the equation (III) is quite satisfactory. Still better agreement can be attained by properly choosing the ionic diameters. In the solution the ionic radius gives the average distance of closest approach between oppositely charged ions. The observed higher values may be explained by assuming that at higher concentrations ionic diameters increase somewhat due to hydration and also to the fact that the average distance of closest approach (between oppositely charged ions) become greater due to mutual repulsion of like charges. Moreover, the calculated values will give higher results if we take into account the change of dielectric constant with concentration. In addition, the effects of secondary forces, which have been neglected, should be considered at higher concentrations but their influence is to decrease the calculated values. All these factors give the resultant values observed. The data, however, show that these are really of secondary importance.

Tables III-V give the relevant data for the alkali halides. It will be seen that the deviations are greater at higher concentrations and they occur in the order  $I^- > Br^- > Cl^-$ . This is quite in order with the increased polarisability of the ions.

TABLE III

Mean activity coefficients at 25°.

Conc.	CsCl $a_+ = 1.67\text{\AA}$ $a_- = 1.81\text{\AA}$		RbCl $a_+ = 1.48\text{\AA}$		KCl $a_+ = 1.33\text{\AA}$		KCl $a_+ = 2.76\text{\AA}$	NaCl $a_+ = 3.2\text{\AA}$	
	obs. (molal)	Calc. (molar)	obs.	calc.	obs.	calc.	calc.	obs.	calc.
0.01	—	0.9239	—	0.9237	0.9221 0.899	—	0.9251	0.903 0.9221	0.9255
1.0	0.543	0.5699	0.583	0.5658	0.605 0.6341	0.5580	0.6222	0.658 0.6891	0.6483
4.0	0.474	0.4462	0.541	0.4292	0.581	0.4170	0.5666	0.792	0.6220

TABLE IV

Mean activity coefficients at 25°.

Conc.	CsBr $a_- = 1.96\text{\AA}$		RbBr		KBr $a_+ = 1.33\text{\AA}$		KBr $a_+ = 2.76\text{\AA}$	NaBr	
	Obs. (molal)	Calc. (molar)	obs.	calc.	obs.	calc.	calc.	obs.	calc.
0.01	—	0.9239	—	0.9239	—	—	0.9251	—	0.9258
1.0	0.537	0.5765	0.579	0.5723	0.617	0.5644	0.6296	0.687	0.6558
4.0	0.460	0.4614	0.517	0.4435	0.625	0.4307	0.5853	0.938	0.6425

TABLE V

Mean activity coefficients at 25°.

Conc.	CaI $a_- = 2.19\text{\AA}$		RbI		KI $a_+ = 1.33\text{\AA}$		KI $a_+ = 2.76\text{\AA}$	NaI	
	obs. (molal)	calc. (molar)	obs.	calc.	obs.	calc.	calc.	obs.	calc.
0.01	—	0.9241	—	0.9241	—	—	0.9253	—	0.9260
1.0	0.532	0.5866	0.575	0.5825	0.646	0.5744	0.6404	0.739	0.6673
4.0	—	0.4850	0.517	0.4665	0.678	0.4530	0.6159	—	0.6761

Again Debye's equation cannot offer any explanation for the values of activity coefficients being greater than unity, but the equation (III) may give such values at higher concentrations if the values of the ionic diameters are sufficiently large. Tables VI and VII and Figs. 3 and 4 show the values of  $\gamma_{\pm}$  and  $\gamma_A$  where the ionic radii of  $R^+$  and  $A^-$  have been taken to be  $5.0 \text{ \AA}$ . For comparison the observed values of activity coefficients of NaCl and HCl have been included. The nature and slope of the curves show striking similarity:

FIG. 3

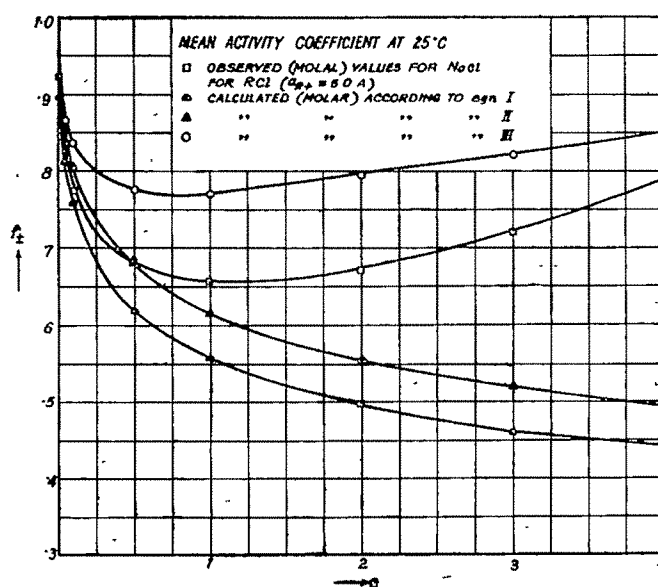


TABLE VI

Mean activity coefficients of RCl at 25°.

Conc.	Observed (molal) NaCl	Calculated (molar) ( $a_{\pm} = 5.0 \text{ \AA}$ )		
		I	II	III
0.01	0.922*	0.8981	0.9260	0.9270
0.05	0.842*	0.8093	0.8535	0.8672
0.1	0.778, 0.798*	0.7575	0.8091	0.8345
0.5	0.682	0.6167	0.6792	0.7734
1.0	0.658	0.5546	0.6167	0.7716
2.0	0.671	0.4967	0.5549	0.7945
3.0	0.720	0.4659	0.5201	0.8215
4.0	0.792	0.4453	0.4968	0.8506

FIG. 4

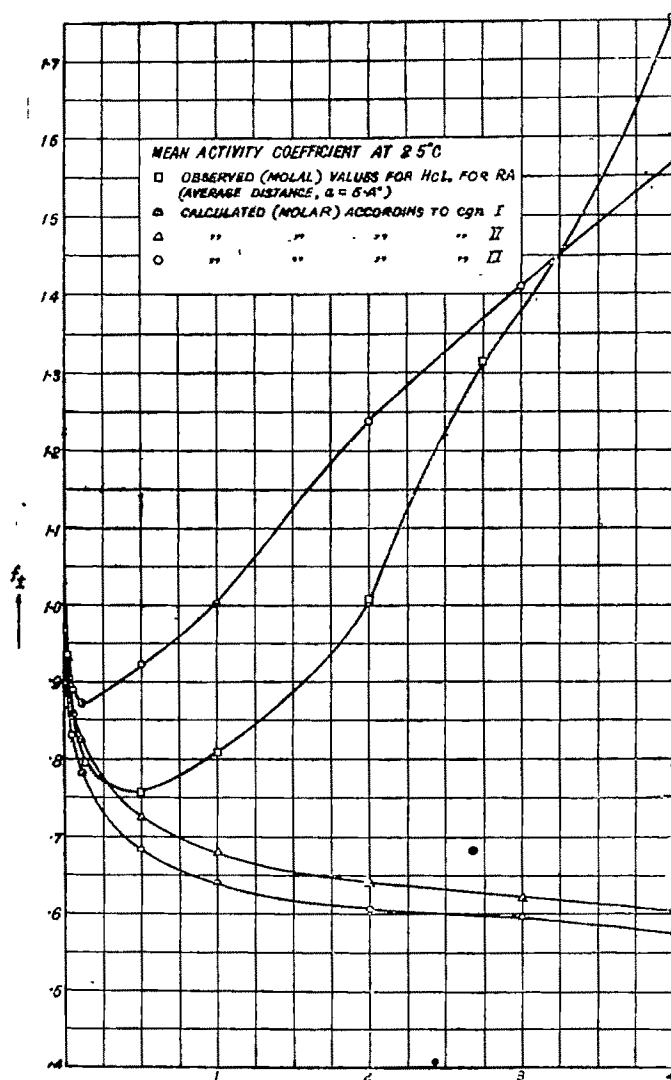


TABLE VII

Mean activity coefficients of RA at 25°.

Conc.	Observed (molal) HCl.	Calculated average distance $i.e., a_{\pm} = a_{\pm} = 5 \text{ \AA}$		
		I	II	III
0.01	0.9048	0.9005	0.9285	0.9340
0.05	0.8304	0.8254	0.8632	0.8804
0.1	0.7964	0.7834	0.8254	0.8743
0.5	0.7571	0.6816	0.7249	0.9247
1.0	0.8030	0.6418	0.6813	1.035
2.0	1.009	0.6071	0.6425	1.238
3.0	1.316	0.5898	0.6112	1.410
4.0	1.762	0.5788	0.6071	1.573

For polyvalent electrolytes, however, the agreement is not so satisfactory. Tables VIII and IX and Figs. 5 and 6 record the values for  $\text{BaCl}_2$  and  $\text{LaCl}_3$  solutions. The crystallographic values of ionic diameters have been used. Here also equation (III)

FIG. 5

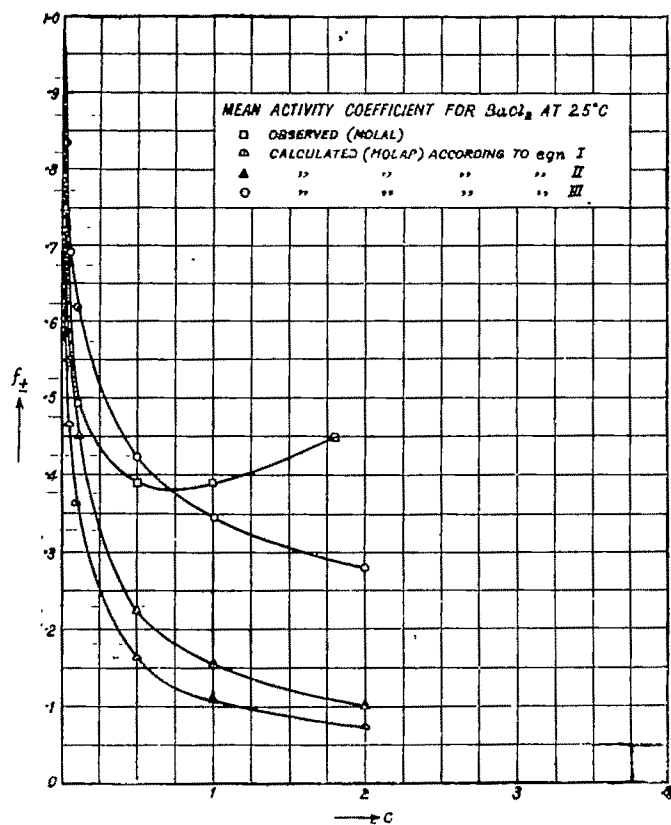
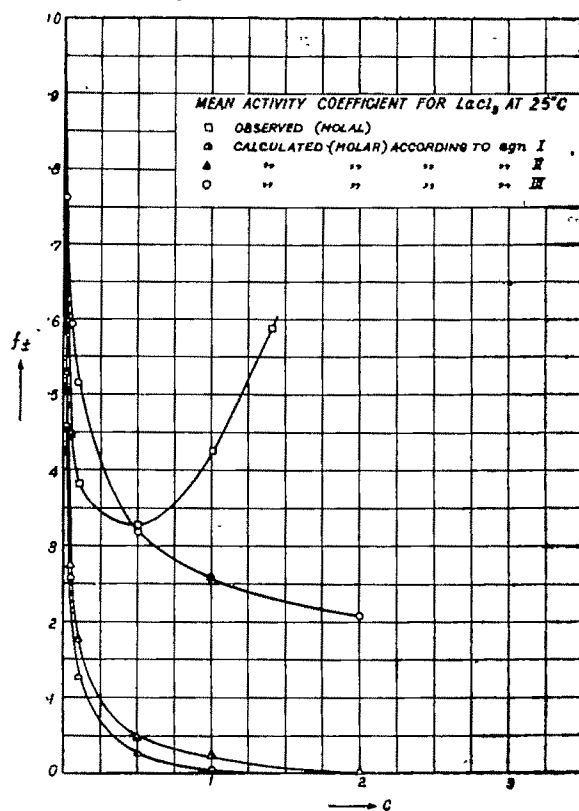


TABLE VIII

Mean activity coefficients of  $\text{BaCl}_2$  at 25°.

Conc.	Observed (molal).	Calculated (molar) ( $a_+ = 1.31\text{\AA}$ ).		
		I	II	III
0.01	0.723	0.6874	0.7521	0.8360
0.05	0.554	0.4652	0.5521	0.6923
0.1	0.492	0.3621	0.4495	0.6189
0.5	0.390	0.1641	0.2258	0.4224
1.0	0.392	0.1087	0.1545	0.3452
2.0	(1.8 → 0.450)	0.0711	0.1021	0.2823

FIG 6



approximates more closely to the observed values. Below the normal concentration the calculated figures give higher values, while above it they are smaller than the observed ones. The higher values may possibly be due to the effects of secondary forces, e.g., forces of polarisation, forces of interaction between the solvent and the

TABLE IX

Mean activity coefficients\* of  $\text{LaCl}_3$  at  $25^\circ$ .

Conc.	Observed (molal).	Calculated (molar) ( $a_+ = 1.06\bar{A}$ ).		
		I	II	III
0.01	0.637	0.4567	0.5320	0.7630
0.05	0.447	0.2066	0.2737	0.5923
0.1	0.383	0.1254	0.1778	0.5124
0.5	0.328	0.0274	0.0446	0.3183
1.0	0.424	0.0070	0.0215	0.2557
2.0	(1.4 $\rightarrow$ 0.587)	0.0059	0.0057	0.2088

solute etc., which are likely to be of more importance for ions of higher valencies, being neglected. The deviation at higher concentrations may be ascribed, in addition to the effects of these secondary forces, to the factors mentioned above, notably due to the increased average distance between the ions caused by the repulsive forces of like charges of higher valencies and to the change in the dielectric constant at higher concentrations.

DEPARTMENT OF PHYSICAL CHEMISTRY,  
UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,  
CALCUTTA.

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# PRODUCTION OF THE JOSHI EFFECT IN OXYGEN UNDER SILENT ELECTRIC DISCHARGE. PART VII. INFLUENCE OF FREQUENCY FILTERS, RESISTIVE AND CAPACITATIVE CHANGES, AND NATURE OF THE A. C. INDICATOR

BY S. R. MOHANTY

The Joshi effect  $\Delta i$  in oxygen enclosed in a Siemens' tube at 27 mm. Hg (20°) pressure and excited over 0.5-3 kV (r. m. s.) of 50 cycles frequency has been studied, ( $i$ ) in different components of the discharge current  $i$ ; ( $ii$ ) under 1 to 10 k $\Omega$  serial (ohmic) resistances  $R$  in L. T.; ( $iii$ ) with various capacitances, 0.00025 to 0.001  $\mu$ F in series with, and 0.0001 to 0.01  $\mu$ F across, the detector, in L. T.; ( $iv$ ) with Cambridge A. O. micro-ammeter, Westector 'cold' rectifier, vacuo-junction, diode, triode and pentode used for observing  $i$ .

$i$  consists of high frequency  $i_{HF}$ , low frequency  $i_{LF}$  and the supply frequency component  $i_s$ . At constant applied potential  $V$ , the net effect  $\Delta i$  and the proportionate effect  $\% \Delta i$  are larger for filtered  $i_{HF}$  than for filtered  $i_{LF}$ . The H. F. region of  $i$  is the chief seat of the phenomenon.

$R$  decreases  $i$ ,  $\Delta i$  and  $\% \Delta i$ ; diminution, in each case, is more pronounced at small rather than at large values of  $R$ . The corresponding  $V$  across the ozoniser, determined electrostatically, is, however, not affected. Inhibition due to  $R$  is attributed, following Joshi, to preferential damping of the H. F. components of  $i$ .

A serial capacitance, in between the L. T. of discharge tube and detector, admits preferentially the H. Fs., and therefore, increases  $\% \Delta i$ . This last is reduced by a capacitance added across the detector, since now the capacitance by-passes the H.Fs.

The 'threshold potential'  $V_m$  is not altered by a change in the mode of current detection.  $\Delta i$  is highest with an inductively fed pentode, and lowest with a Westector 'cold' rectifier. Potential variation of  $\Delta i$  and  $\% \Delta i$  is similar in all the cases. With a thermionic tube detector,  $\Delta i$  is always higher with the method of inductive coupling than with that of resistive coupling. With a triode,  $\Delta i$  is higher with anode bend than with grid leak detection. A positive effect  $+\Delta i$  is observed with valve detectors at low applied  $V$ , decreases with  $V$ , and rapidly changes sign above  $V_m$ .  $+\Delta i$  is not observed under identical conditions with a vacuo-junction. The selectivity in response of the various detectors to different frequencies in the spectrum of  $i$  is considered to be responsible for the observed variations in  $\Delta i$ .

The present communication, which is an extension of the preliminary observations of the author (*Proc. Indian Sci. Cong.*, 1947, Part III, *Phys. Sec.*, Abst. No. 14) and of the author and Kamath (*ibid.*, 1947, Part III, *Phys. Sec.*, Abst. No. 15), reports results on the Joshi effect in oxygen, in the high and the low frequency components of the discharge current, under resistive and capacitive changes in the L. T. circuit, and with different modes of current detection, including the production of a positive effect, i. e., a current gain under irradiation, with thermionic tube detectors.

## EXPERIMENTAL

The general experimental arrangement and the circuit employed are shown in Fig. 1. The electrical discharge was produced in the annular space of a



Siemens' type (glass) ozoniser filled with purified oxygen at 27 mm. (20°) Hg pressure. The exciting potential  $V$  was varied in the range 0.5-3 kV (r.m.s.) ; its frequency was 50 cycles per second. The discharge current  $i$ , after rectification, was observed, in dark  $i_D$  and under light  $i_L$ , on a sensitive D. C. mirror

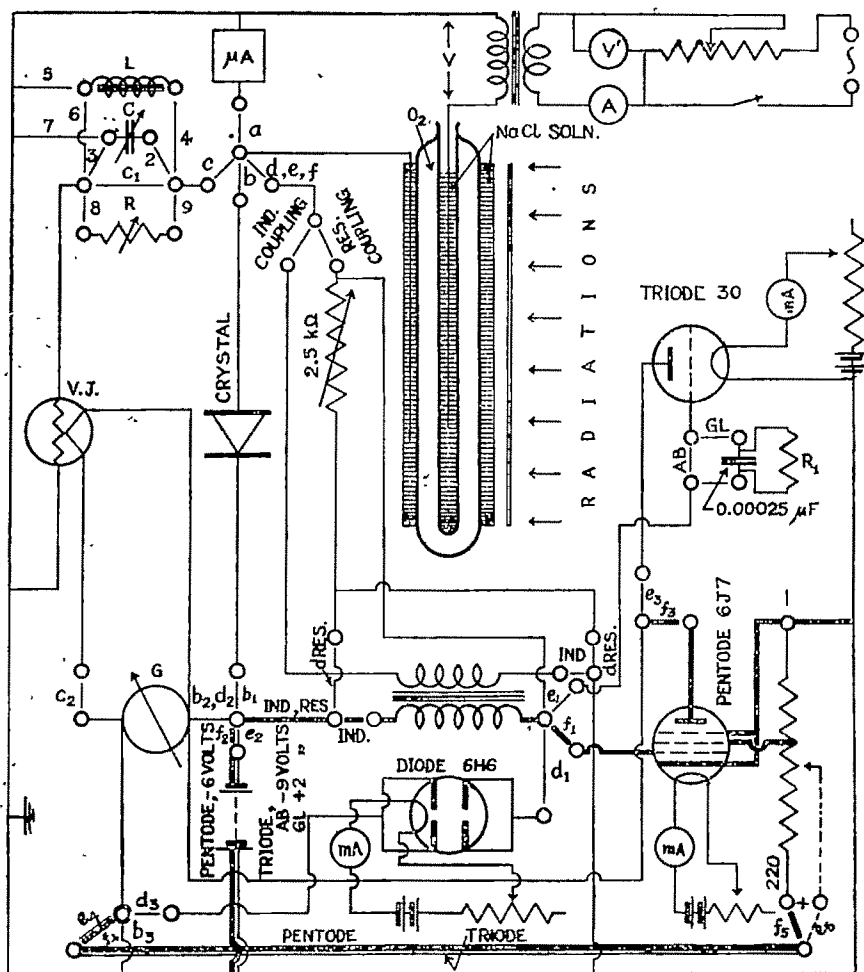


FIG. 1

galvanometer  $G$  properly shunted. The source of light consisted of a battery of three 200 watt incandescent (glass) bulbs run at 200 volts. The mode of observation of  $\Delta i$  was similar to that described in Part I (Mohanty and Kamath, this *Journal*, 1948, 25, 405).

For the study of  $\Delta i$  in different components of  $i$  (Table I), and of the influence of resistive (Table II) and capacitive (Tables III, IV) changes, a low resistance (25 $\Omega$ ) vacuo-junction (V.J., Fig. 1) was used as detector. The discharge current, which consists of high frequencies H. F., low frequencies L. F. and the supply frequency component (*vide infra*), was fed first directly into the

detector through  $c$  and  $c_1$  (Fig. 1), and  $\Delta i$  observed. A capacitance  $C$  of  $0.0001 \mu F$  was next introduced serially in between the L.T. terminal of the discharge tube and the vacuo-junction via 2 and 3 ( $c_1$  having been disconnected). It admitted preferentially the H.F. and inhibited the L.F., the latter were bypassed by the iron-core inductance  $L$  of about 200 henrys (which inhibited the L.F.), connected through 4 and 5. Finally, the L.F. were filtered into the detector through  $L$ , put in series in L.T. via 4 and 6, besides  $C$  across the vacuo-junction through 2 and 7. The effect was also studied under capacitive and resistive changes in the L.T. circuit. Capacitance introduced in series ( $C_2$ ) in between the L.T. terminal of the discharge tube and the detector was varied over  $0.00025 - 0.001 \mu F$ , and that put across ( $C_1$ ) the detector from  $0.0001$  to  $0.01 \mu F$ . The ohmic resistance  $R$  connected serially in L.T. was varied over  $1-10 \text{ k}\Omega$ ; it was of Dubilier type, non-inductive and sensibly non-capacitative.

A comparative study of  $\Delta i$  was next made (Table V) with the following detectors used for observing  $i$ :

(a) *Cambridge A. C. micro-ammeter* ( $\mu A$ , Fig 1).—This was a full-wave copper-copper oxide rectifier, and was introduced in series in L.T.

(b) *Westector 'cold' rectifier*.—This was a half-wave crystal detector. It was connected, in series with the galvanometer  $G$ , between the L.T. terminal of the ozoniser and earth

(c) *Cambridge vacuo-junction*.—The one used had a low heater resistance ( $25 \Omega$ ). This was connected to the galvanometer  $G$ . The arrangement was appreciably current sensitive, since the corresponding galvanometer deflections are proportional to the square of the current flowing through the ozoniser.

(d) *Double diode 6H6 (RCA)*.—This was used as a half-wave rectifier. For this purpose, the two plates, as also the two cathodes, were short-circuited. The filament of the thermionic tube was heated at 270 mA obtained from a battery of three 2 volt accumulators. In one series of observations, the current flowing through the ozoniser was passed through the primaries of a 3:4 Bell type iron-core transformer. The secondaries of this transformer were connected to the plates and the cathodes of the valve through the galvanometer  $G$ . In another set of observations, the input to the diode was tapped from across a non-inductive and sensibly non-capacitative Dubilier type resistance of  $2.5 \text{ k}\Omega$  introduced serially in L.T.

(e) *Triode 30 (RCA)*.—This was used as (i) an anode bend detector, and (ii) as a grid leak detector. The thermionic tube was fed both inductively and resistively from the L.T. The filament of the valve was heated with a current of 56 mA drawn from a 2 volt storage cell. For (i), the grid was given a negative bias of 9 volts obtained from dry cells. The positive terminal of the grid bias battery and the filament of the valve were earthed. The plate was maintained at +90 volts obtained from 220 volt, D.C. mains by means of a potentiometric arrangement. The galvanometer  $G$  was introduced in the plate circuit.

TABLE I

*The Joshi effect in oxygen in different components of the discharge current.*

$pO_2 = 27 \text{ mm}(20^\circ)$ . Temp.  $= 33^\circ$ . Frequency of A. C. supply  $= 50 \text{ cyc./sec}$ . Detector  $=$  Vacuo-junction. Source of radiations  $=$  Three 300 volt, 200 watt (glass) bulbs 22 cm. from the ozoniser.

V (kV, r.m.s.)	$i_D$			$i_L$			$\Delta i$			$\% \Delta i$		
	L.T.	H.F.	L.F.	L.T.	H.F.	L.F.	L.T.	H.F.	L.F.	L.T.	H.F.	L.F.
0.67	12.69	9.64	2.45	7.81	5.92	1.78	4.88	3.72	0.72	38.5	38.6	39.4
0.98	15.18	11.23	3.87	10.3	7.48	3.08	4.88	3.75	0.79	31.9	33.4	20.4
1.3	13.98	10.58	4.58	10.4	7.55	3.87	3.56	3.08	0.71	25.5	28.6	15.5
1.47	14.07	10.35	5.24	10.86	7.68	4.69	8.21	2.97	0.55	22.8	25.8	10.5
1.87	14.11	10.2	6.16	11.45	7.94	5.70	2.66	2.26	0.46	18.9	22.2	7.5
2.27	14.45	9.8	6.93	12.28	8.06	6.71	2.17	1.74	0.22	15.0	17.8	8.2
2.67	15.00	9.8	8.19	13.30	8.25		1.70	1.55		11.3	15.8	

TABLE II

*Influence of resistive impedance on the Joshi effect in oxygen.* $pO_2 = 27$  mm (20°). Temperature =  $-31^\circ$ . Frequency of A.C. supply = 50 cye./sec.

Detector = Vacuo-junction. Source of radiations = Three 200 volt, 200 watt (glass) bulbs, 15 cm. from the ozoniser.

$\frac{R(k\Omega)}{V}$	0.	1.	2.5.	5.	7.5.	10.
(kV, r.m.s.)						
0.67	$i_D$	11.92	6.48	5.89	5.00	4.58
	$i_L$	6.93	4.12	3.46	3.16	2.83
	$\Delta i$	4.99	2.36	1.93	1.84	1.75
	% $\Delta i$	41.8	36.4	35.8	36.8	38.2
0.93	$i_D$	13.28	7.48	6.71	6.25	5.92
	$i_L$	9.11	5.39	5.2	4.9	4.69
	$\Delta i$	4.15	2.09	1.51	1.35	1.23
	% $\Delta i$	31.3	27.9	22.5	21.6	20.8
1.2	$i_D$	13.15	7.75	6.63	6.33	6.00
	$i_L$	9.75	6.33	5.57	5.29	5.1
	$\Delta i$	3.40	1.42	1.06	1.04	0.9
	% $\Delta i$	25.9	18.3	16	16.4	15.0
1.47	$i_D$	12.78	7.87	6.86	6.58	6.16
	$i_L$	10.05	6.78	6.08	5.75	5.57
	$\Delta i$	2.71	1.09	0.78	0.83	0.59
	% $\Delta i$	21.2	13.9	11.4	12.6	9.6
1.87	$i_D$	13.00	8.43	7.42	7.07	6.78
	$i_L$	10.77	7.55	6.86	6.56	6.33
	$\Delta i$	2.23	0.88	0.56	0.51	0.45
	% $\Delta i$	17.2	10.4	7.5	7.2	6.6
2.27	$i_D$	13.48	9.22	8.54	8.12	7.81
	$i_L$	11.66	8.66	8.06	7.63	7.42
	$\Delta i$	1.80	0.56	0.48	0.50	0.39
	% $\Delta i$	13.4	6.1	5.6	6.2	5
2.67	$i_D$	14.29	10.35	9.59	9.27	
	$i_L$	12.92	9.95	9.27	9.00	
	$\Delta i$	1.37	0.40	0.32	0.27	
	% $\Delta i$	9.6	3.9	3.3	2.9	

TABLE III

*Influence of capacitance, introduced in L. T. in series with the detector, on the Joshi effect in oxygen.*

$pO_2 = 27 \text{ mm (20°)}$ . Temperature =  $83^\circ$ . Frequency of A. C. supply = 50 cyc./sec.  
 Detector = Vacuo-junction. Source of radiations = Three 270 volt, 200 watt (glass) bulbs,  
 22 cm. from the ozoniser.

$O_2 (\mu F)$		0.	0.00025.	0.0005	0.001.
$\frac{\quad}{V}$					
(kV, r.m.s.)					
0.67	$i_D$	10.77	5.00	7.87	6.93
	$i_L$	6.25	2.83	4.24	4.24
	$\Delta i$	4.52	2.17	3.63	2.69
	$\% \Delta i$	42	43.4	46.1	38.8
0.93	$i_D$	12.61	8.25	10.81	11.36
	$i_L$	8.60	5.39	6.93	7.14
	$\Delta i$	4.01	2.84	3.88	4.22
	$\% \Delta i$	31.8	34.4	35.9	37.2
1.2	$i_D$	12.13	8.66	10.86	10.95
	$i_L$	9.00	5.66	7.14	7.43
	$\Delta i$	3.13	3.00	3.72	3.47
	$\% \Delta i$	25.8	34.6	34.3	31.7
1.47	$i_D$	11.84	8.43	10.44	10.68
	$i_L$	9.27	5.83	7.12	7.62
	$\Delta i$	2.57	2.60	3.02	3.06
	$\% \Delta i$	21.7	30.8	28.9	28.7
1.87	$i_D$	11.79	7.87	10.1	10.44
	$i_L$	10.00	5.93	7.62	7.87
	$\Delta i$	1.79	1.95	2.48	2.57
	$\% \Delta i$	15.2	24.8	24.6	24.6
2.27	$i_D$	12.46	7.81	9.33	9.59
	$i_L$	10.77	6.00	7.62	7.87
	$\Delta i$	1.69	1.81	1.71	1.72
	$\% \Delta i$	13.6	23.2	18.3	17.9
2.67	$i_D$	12.96	7.35	9.59	
	$i_L$	11.06	6.00	8.06	
	$\Delta i$	1.90	1.35	1.53	
	$\% \Delta i$	7.7	18.4	16	

TABLE IV

*Variation with capacitance, introduced in L.T. in parallel to the detector, of the Joshi effect in oxygen.*

$pO_2 = 27 \text{ mm } 20^\circ$ . Temperature  $-32^\circ$ . Frequency of A.C. supply = 50 cye./sec. Detector = Vacuo-junction. Source of radiations = Three 200 volt, 200 watt (glass) bulbs, 22 cm. from the ozoniser.

$C_1 \text{ (F}\mu\text{)}$ $\swarrow$ V		0	0.0001,	0.00025,	0.0005,	0.001,	0.005,	0.01.
(kV, r.m.s.)								
0.67	$i_D$	11.63	12.46	12.09	10.15	9.85	9.00	8.60
	$i_L$	6.63	7.28	7.21	6.08	5.67	5.34	5.1
	$\Delta i$	4.9	5.18	4.88	4.07	4.28	3.66	3.5
	$\% \Delta i$	42.5	41.6	40.4	40.1	43.5	40.7	40.7
0.93	$i_D$	12.04	13.08	12.49	10.63	10.49	9.54	9.33
	$i_L$	8.43	9.00	8.66	7.68	7.62	6.93	6.76
	$\Delta i$	3.61	4.08	3.83	2.95	2.87	2.61	2.58
	$\% \Delta i$	30	31.2	30.7	27.8	27.4	27.4	27.7
1.2	$i_D$	11.62	12.61	12.28	10.58	10.40	9.33	9.22
	$i_L$	8.66	9.27	9.00	8.06	7.94	7.21	7.00
	$\Delta i$	2.96	3.34	3.28	2.52	2.46	2.12	2.22
	$\% \Delta i$	25.5	26.5	26.7	23.8	23.7	22.7	24.1
1.47	$i_D$	11.75	12.69	12.21	10.54	10.40	9.43	9.22
	$i_L$	9.38	9.85	9.61	8.66	8.49	7.84	7.52
	$\Delta i$	2.37	2.84	2.57	1.88	1.91	1.59	1.70
	$\% \Delta i$	20.2	22.4	21.0	17.8	18.4	16.9	18.4
1.87	$i_D$	12.04	13.75	12.53	11.00	10.81	9.8	9.54
	$i_L$	10.15	10.86	10.63	9.43	9.38	8.60	8.37
	$\Delta i$	1.89	2.29	1.90	1.57	1.43	1.2	1.17
	$\% \Delta i$	15.7	17.4	15.2	14.3	13.2	12.8	12.3
2.27	$i_D$	12.78	13.61	13.23	11.83	11.63	10.63	10.35
	$i_L$	11.09	11.70	11.45	10.14	10.30	9.54	9.33
	$\Delta i$	1.64	1.94	1.78	1.69	1.32	1.09	1.02
	$\% \Delta i$	12.9	14.2	13.5	11.7	11.4	10.3	9.9
2.67	$i_D$	13.68	14.53	14.25	12.78	12.61	11.84	11.62
	$i_L$	12.41	13.04	12.76	11.79	11.62	11.00	10.77
	$\Delta i$	1.27	1.49	1.49	7.4	0.99	0.84	0.85
	$\% \Delta i$	9.3	10.3	10.5	9.4	7.9	7.1	7.3

TABLE V

*The Joshi effect in oxygen with different modes of current detection.*

$pO_2 = 27$  mm. ( $20^\circ$ ). Temperature =  $22^\circ - 25^\circ$ . Frequency of A. C. supply = 50 cyc./sec.  
Source of radiations = Three 200 volt, 200 watt (glass) bulbs, 22 cm. from the ozoniser.

V (kV, r.m.s.).	Cambridge $\mu A$ . Westector rectifier. Vacuo-junction.	Diode 6H6 (RCA)		Triode 80 (RCA)				Pentode 6J7 (RCA)	
				Anode bend		Grid leak			
		I.C.	R.C.	I.C.	R.C.	I.C.	R.C.	I.C.	R.C.
0.53	$i_D$	1.41	—	9	—	—	—	—	—
	$i_L$	1.41	—	9	—	—	—	—	—
	$\Delta i$	—	—	—	—	—	—	—	—
	% $\Delta i$	—	—	—	—	—	—	—	—
0.56	$i_D$	1.43	—	10	—	—	—	—	—
	$i_L$	1.43	—	12	—	—	—	—	—
	$\Delta i$	—	—	+2	—	—	—	—	—
	% $\Delta i$	—	—	+20	—	—	—	—	—
0.59	$i_D$	6.44	8	19	—	—	—	41	—
	$i_L$	6.70	42	21	—	—	—	83	—
	$\Delta i$	0.74	+39	+2	—	—	—	+42	—
	% $\Delta i$	17.8	+1300	+10.5	—	—	—	+102	—
0.61	$i_D$	8.57	54	26	40	—	—	81	—
	$i_L$	7.11	63	30	151	—	—	130	—
	$\Delta i$	1.46	+9	+4	+111	—	—	+89	—
	% $\Delta i$	17.0	+16.7	+15.4	+278	—	—	+48.3	—
0.64	$i_D$	10.84	84	36	164	—	—	125	—
	$i_L$	8.28	84	39	245	—	—	144	—
	$\Delta i$	2.56	—	+3	+81	—	—	+19	—
	% $\Delta i$	23.6	—	+8.3	+50	—	—	+15.2	—
0.67	$i_D$	11.85	128	55	298	—	—	212	—
	$i_L$	8.86	101	51.5	298	—	—	165	—
	$\Delta i$	2.99	27	3.5	—	—	—	47	—
	% $\Delta i$	25.2	21.1	6.4	—	—	—	22.2	—
0.69	$i_D$	12.06	146	63	375	—	—	240	—
	$i_L$	9.57	114	59	312	—	—	181	—
	$\Delta i$	2.49	32	4	63	—	—	59	—
	% $\Delta i$	20.7	21.9	6.4	16.8	—	—	24.6	—
0.72	$i_D$	12.27	147	71	386	—	—	262	—
	$i_L$	9.62	112	67	292	—	—	188	—
	$\Delta i$	2.65	35	4	94	—	—	74	—
	% $\Delta i$	21.6	23.8	5.6	24.4	—	—	28.2	—
0.75	$i_D$	12.48	145	70.5	351	—	—	270	—
	$i_L$	9.67	112	73	272	—	—	193	—
	$\Delta i$	2.81	33	8.5	79	—	—	77	—
	% $\Delta i$	22.5	22.8	4.6	22.5	—	—	28.5	—
0.77	$i_D$	12.78	147	81	335	—	—	280	—
	$i_L$	9.97	108	75	264	—	—	195	—
	$\Delta i$	2.81	39	8	71	—	—	85	—
	% $\Delta i$	22	26.5	3.7	21.2	—	—	30.4	—

(The above observations were made with a comparatively sensitive voltmeter for measuring V%).

TABLE V ( *contd.* )

V (kV, r.m.s.)		Cambridge $\mu$ A.	Westector rectifier.	Vacuo-junction.	Diode 6H6 (ROA)		Triode 80 (RCA)				Pentode 6J7 (RCA)	
							Anode bend		Grid leak			
					I.O.	R.O.	I.O.	R.O.	I.O.	R.O.	I.O.	R.O.
0.67	$i_D$	8	11	4.00	68	55	105	89	179	30	146	48
	$i_L$	8	11	3.08	50	51.5	82	35	141	27	104	48
	$\Delta i$	-	-	0.92	18	3.5	23	4	38	3	42	5
	% $\Delta i$	-	-	23	28.5	6.4	21.9	10.3	21.2	10.0	28.8	10.4
0.8	$i_D$	7.5	24	4.9	181	86	147	75		57	188	68
	$i_L$	0.5	23	3.81	96	83	103	71		56	118	64
	$\Delta i$	1.0	1	1.09	38	3	44	4		1	70	4
	% $\Delta i$	13.3	4.2	22.2	28.3	3.5	29.9	5.3		1.8	37.2	5.9
0.93	$i_D$	9.5	34	4.95	133	122	112	105	173	81	182	94
	$i_L$	9.0	33	4.00	99	120	102	103	165	81	118	91
	$\Delta i$	0.5	1	0.95	34	2	40	2	8	—	64	3
	% $\Delta i$	5.3	2.9	19.2	25.6	1.6	23.2	1.9	4.6	—	35.2	3.2
1.07	$i_D$	12.5	47	5.1	129	158	130	145		96	179	120
	$i_L$	12.0	43.5	4.47	105	158	96	143		96	120	117
	$\Delta i$	0.5	0.5	0.63	24	—	34	2		—	59	3
	% $\Delta i$	4.0	1.1	12.4	18.6	—	26.2	1.4		—	33	2.5
1.2	$i_D$	16	60	5.29	127	201.5	129	185	179	110	175	148
	$i_L$	15.5	60	4.69	107	201.5	101	185	171	110	124	148
	$\Delta i$	0.5	—	0.60	2	—	28	—	8	—	61	—
	% $\Delta i$	3.1	—	11.8	15.7	—	21.7	—	4.5	—	29.2	—
1.33	$i_D$	19.5	74	5.48	127	251	135	235		125	170	174
	$i_L$	19.5	74	4.9	111.5	251	108	235		125	124	174
	$\Delta i$	—	—	0.58	15.5	—	27	—		—	46	—
	% $\Delta i$	—	—	10.6	12.2	—	20.0	—		—	27.1	—
1.47	$i_D$	23.5	86.5	5.75	129		151		183		169	
	$i_L$	23.5	86.5	5.29	116		126		178		130	
	$\Delta i$	—	—	0.46	13		25		5		39	
	% $\Delta i$	—	—	8	10.1		16.6		2.7		23.1	
1.6	$i_D$	28.5	102.5	5.96	130		164				175	
	$i_L$	28.5	102.5	5.57	121		145				140	
	$\Delta i$	—	—	0.39	9		19				35	
	% $\Delta i$	—	—	6.5	6.9		11.6				20.0	



TABLE V (contd.)

$V$ ( $\frac{1}{2}V$ , r.m.s.)		Cambridge $\mu A$ .	Westector rectifier.	Vacuo-junction.	Diode 6H6 (RCA)'		Triode 90 (RCA)		Pentode 6J7 (RCA)
					I.C. R.C.		Anode bend	Grid leak	
							I.C. R.C.	I.C. R.C.	I.C. R.C.
1.73	$i_D$	34	116	6.29	135		183	183	190
	$i_L$	34	116	5.92	127		163	178	156
	$\Delta i$	—	—	0.37	8		20	5	34
	$\% \Delta i$	—	—	5.9	5.9		10.9	2.7	17.9
1.87	$i_D$	40	130	6.63	139		206		200
	$i_L$	40	130	6.29	133.5		186		166
	$\Delta i$	—	—	0.34	5.5		20		34
	$\% \Delta i$	—	—	5.1	4		9.7		17.0
2	$i_D$	46	144	7.00	145		226	185.5	207
	$i_L$	46	144	6.71	140		207	181.5	174
	$\Delta i$	—	—	0.29	5		19	4	38
	$\% \Delta i$	—	—	4.1	3.4		8.4	2.2	15.9
2.13	$i_D$	58	159	7.35	152		249		217
	$i_L$	58	159	7.14	148.5		237		189
	$\Delta i$	—	—	0.21	3.5		12		28
	$\% \Delta i$	—	—	2.9	2.3		4.8		12.9
2.27	$i_D$	60.5	173	7.81	159		274	186	224
	$i_L$	60.5	173	7.65	157		259	182	197
	$\Delta i$	—	—	0.16	2		15	4	27
	$\% \Delta i$	—	—	2.0	1.3		5.5	2.2	12.1
2.4	$i_D$	68	188	8.31	169		300		229
	$i_L$	68	188	8.06	167.5		290.5		205.5
	$\Delta i$	—	—	0.25	1.5		9.5		23.5
	$\% \Delta i$	—	—	3.0	0.9		3.2		10.8
2.53	$i_D$	77.5	198	8.83	181		323	186	235
	$i_L$	77.5	198	8.57	180		314	182	212
	$\Delta i$	—	—	0.26	1		9	4	23
	$\% \Delta i$	—	—	2.9			2.8	2.2	9.8
2.67	$i_D$	86.5	209	9.33	192		348		240
	$i_L$	86.5	209	9.14	191		340		218
	$\Delta i$	—	—	0.19	1		8		22
	$\% \Delta i$	—	—	2.0			2.3		9.2
2.8	$i_D$	94.5	226.5	9.77	203		374	186	244
	$i_L$	94.5	226.5	9.7	202		370	184	225
	$\Delta i$	—	—	0.07	1		4	2	19
	$\% \Delta i$	—	—	0.7			1.1	1.1	7.8

(I.C.=Inductive coupling; R.C.=Resistive coupling)

For grid leak detection, a  $0.00025 \mu\text{F}$  capacitance shunted with Dubilier type resistances  $R_1$  was introduced in the grid circuit. The grid was returned to the positive of the two volt filament cell. The negative of the cell (and hence also the filament) was earthed. The plate was given a positive potential of 40 volts. The anode current was determined with the galvanometer G. A series of observations was made with  $R_1$  varied over 1-5 Ma.

(f) *Pentode 6J7 (RCA).*—The tube was coupled with the L.T., both inductively and resistively. The control grid was given a negative bias of 6 volts. The suppressor and the cathode of the thermionic tube were earthed. The plate was given a positive potential of 220 volts, and the screen of 100 volts. The filament was heated at 280 mA obtained from a battery of 3 storage cells. The current in the plate circuit was observed with the galvanometer G.

## DISCUSSION

*The Joshi Effect in Different Components of the Discharge Current.*—Results in Table I show that similar to the observations of Joshi (*Curr. Sci.*, 1945, 14, 67) in chlorine, both  $\Delta i$  and  $\% \Delta i$  in oxygen are greater for the high than for the low frequency components of  $i$ . Further, it is seen that whilst  $\Delta i$  for the total unfiltered current is greater than that for H.F., the relative effect  $\% \Delta i$  for the latter is sensibly greater than that for the former. Thus e.g., the values for  $\Delta i$  at 1.2 kV for the unfiltered current, the H.F. and the L.F. are respectively 3.56, 3.03 and 0.71; the corresponding values of  $\% \Delta i$  are respectively 25.5, 28.6 and 15.5. Increase of the exciting V reduces progressively both  $\Delta i$  and  $\% \Delta i$  in all the three cases.

The magnitude of  $i$ , both in dark and under irradiation, at a given applied V is in the order: unfiltered  $>$  H.F.  $>$  L.F. Thus e.g., at the above V, its values in dark are respectively 13.96, 10.58 and 4.58.

The oscillographic studies of Joshi (*ibid.*, 1944, 13, 253; *Nature*, 1944, 154, 147) have revealed that  $i$  consists of high frequency  $i_{\text{HF}}$ , low frequency  $i_{\text{LF}}$  and the supply frequency component  $i_s$ . Thus, added vectorially

$$i = i_{\text{HF}} + i_{\text{LF}} + i_s.$$

Under irradiation, there occurs an instantaneous and reversible diminution of the amplitudes of especially the high frequency components of  $i$ , indicating that the latter constitute the chief seat of the  $\Delta i$  phenomenon. That in oxygen as well the Joshi effect preponderates in the H.F. region of  $i$  is evident from the foregoing results.

*Influence of Resistive Impedance.*—From data in Table II, it is seen that both  $i_D$  and  $i_L$ ,  $\Delta i$  and  $\% \Delta i$  are markedly reduced due to a non-inductive resistance R introduced in the L.T. circuit. This inhibition of  $i$ ,  $\Delta i$  and  $\% \Delta i$  due to R is found, in agreement with the observation of Joshi (*Proc. Ind. Acad.*

*Sci.*, 1945, A22, 225) in chlorine, to be more pronounced at small rather than at large values of  $R$ . Thus e.g.,  $i_D$  at 1.2 kV is 13.15 when  $R=0 \Omega$ ; the corresponding values of  $\Delta i$  and  $\% \Delta i$  are respectively 3.4 and 25.9. Increase of  $R$  to 1 k $\Omega$  reduces  $i_D$ ,  $\Delta i$  and  $\% \Delta i$  to 7.75, 1.42 and 18.3 respectively; further increase in  $R$  to 10 k $\Omega$ , however, decreases  $i_D$ ,  $\Delta i$  and  $\% \Delta i$  only to 5.75, 0.85 and 14.8 respectively.

The Siemens' ozoniser (Joshi, *Curr. Sci.*, 1947, 16, 19) is essentially a compound condenser constituted of three serial capacities: two due to the inner and outer electrode walls and a third associated with the gas in the annular space. Above the 'threshold potential'  $V_m$ , the gas breaks down as a dielectric; the corresponding capacity may therefore be considered as a condenser shunted by an ohmic resistance. From general considerations of a oscillatory discharge of a condenser (such as the ozoniser) in a resistive circuit, Joshi (*Proc. Ind. Acad. Sci.*, 1945, A22, 225) showed that  $R$  mainly damped the high frequency components of  $i$ . This was confirmed by his oscillographic studies of  $\Delta i$  under various  $R$ , and the observed reduction in the corresponding aerial current which is predominately H.F. Since the Joshi effect is preferentially incident in the region of high frequencies produced under the discharge (*vide supra*), the observed decrease in  $\Delta i$  and  $\% \Delta i$  due to  $R$  follows.

It is of interest to note that the voltage across the ozoniser, as measured by a Kelvin-White electrostatic voltmeter, does not vary sensibly due to the introduction of  $R$ . This is due to the fact that  $R$ , which is of the order of a few thousand ohms, is very small compared with the resistance of the ozoniser itself.

*Influence of Capacitative Changes.*—In agreement with the general findings of Joshi (*ibid.*, 1945, A22, 225), it is observed (Tables III and IV) that the magnitude of the effect in oxygen is sensibly altered by capacitative changes in the system. The effect of a capacitance is greater when it is added in series than when it is introduced in parallel to the detector.

Whereas  $\Delta i$  without capacitance decreases from 4.52 at 0.67 kV to 1.00 at 2.67 kV,  $\Delta i$  with a serial capacitance  $C_2$  first increases to a maximum at 0.93 kV and then decreases at higher  $V$  (Table III). Thus e. g., with  $C_2 = 0.0005 \mu F$ ,  $\Delta i$  increases from 3.63 at 0.67 kV to a maximum of 3.88 at 0.93 kV, and decreases with further rise in  $V$  to 1.53 at 2.67 kV. It is also seen that with  $C_2 = 0.00025 \mu F$ ,  $\Delta i$  below 1.47 kV is less than that without  $C_2$ ; above 1.47 kV it is the reverse. Thus, values for  $\Delta i$  at 0.93 and 1.87 kV are respectively 4.01 and 1.79 without  $C_2$  and 2.84 and 1.95 with the above capacitance. With higher  $C_2$ , viz., 0.0005 and 0.001  $\mu F$ ,  $\Delta i$  above 0.93 kV is greater than that without  $C_2$ , whereas below 0.93 kV  $\Delta i$  without  $C_2$  is greater. At 0.67 and 1.2 kV, e. g., values for  $\Delta i$  are respectively 4.52 and 3.13 without  $C_2$ , and 3.63 and 3.72 with 0.0005  $\mu F$ . The  $\Delta i$ - $V$  curves for  $C_2 = 0.0005$  and 0.001  $\mu F$  coincide above 1.2 kV.

The relative effect  $\% \Delta i$  is increased markedly due to  $C_2$  (Table III). The effect is most pronounced with the smallest capacitance, viz.,  $0.00025 \mu\text{F}$  and at higher  $V$ . With higher  $C_2$ , viz.,  $0.0005$  and  $0.001 \mu\text{F}$ ,  $\% \Delta i$  is smaller than that with  $0.00025 \mu\text{F}$ . Thus, with  $C_2 = 0, 0.00025, 0.0005$  and  $0.001 \mu\text{F}$ , values for  $\% \Delta i$  at  $2.27 \text{ kV}$  are respectively  $13.6, 23.2, 18.3$  and  $17.9$ , and at  $1.2 \text{ kV}$ ,  $25.8, 34.6, 34.3$  and  $31.7$ . The increase in  $\% \Delta i$  on the introduction of a serial capacitance in the L.T. circuit, provides another proof for the observation that in oxygen, as in chlorine, the Joshi effect preponderates in the high frequency region of  $i$ .

The net effect  $\Delta i$  increases as a result of introduction of a parallel capacitance  $C_1 = 0.0001 \mu\text{F}$  (Table IV). At  $1.2 \text{ kV}$ , e.g.,  $\Delta i$  with and without the above capacitance is respectively  $3.34$  and  $2.96$ . With increase of  $C_1$ ,  $\Delta i$  decreases. It is, at the above  $V$ ,  $3.28$  for  $0.00025 \mu\text{F}$  and  $2.22$  for  $0.01 \mu\text{F}$ .

Since  $i_{\text{HF}}$ , which represents the main seat of the phenomenon, is by-passed by  $C_1$ , a reduction in  $\% \Delta i$  is to be anticipated. This is actually observed (Table IV). For instance, values for  $\% \Delta i$  at  $1.47 \text{ kV}$  with and without  $C_1 = 0.0005 \mu\text{F}$  are respectively  $20.2$  and  $17.8$ . As has been already pointed out, the effect of  $C_1$  added in parallel to the vacuo-junction is small in comparison with that of  $C_2$  introduced in series with the detector.

*The Joshi Effect with Different Modes of Current Detection.*—That  $V_m$ , at which  $i$  increases rapidly with the applied  $V$ , is a fundamental quantity is brought out by the results of these investigations. Despite widely varying methods of current detection, this potential for the ozoniser containing oxygen at a pressure of  $27 \text{ mm. (20°)}$  is a constant quantity of  $0.6 \text{ kV}$ , the other factors, viz., the frequency of the A.C. supply and the temperature, being (sensibly) constant.

From Table V, it is evident that in agreement with the results of earlier work in chlorine (Joshi, *Proc. Indian Sci. Cong.*, 1943, Part II, pp. 70-75; *Curr. Sci.*, 1945, 14, 67; Prasad, *Indian J. Phys.*, 1946, 20, 187) and bromine (Tewari, *ibid.*, 1948, 22, 553) in these laboratories, the magnitude of the Joshi effect in oxygen varies apparently with the mode of current detection. Thus e.g., at  $0.93 \text{ kV}$ ,  $\% \Delta i$  is  $19.2$  with a vacuo-junction. With the two crystal detectors, viz., the Cambridge A.C. micro-ammeter and the Westector rectifier, values for  $\% \Delta i$  at the above  $V$  are comparatively low, being  $5.3$  and  $2.9$  respectively. This is also the case with a diode 6H6 (1.6), a triode 30 (anode bend  $1.9$ ; grid leak  $0.0$ ) and a pentode 6J7 (3.2) coupled resistively, and the triode, fed inductively but used as a grid leak detector (4.6). On the other hand,  $\% \Delta i$  is comparatively high, viz.,  $35.2, 28.2$ , and  $25.6$  when  $i$  is detected respectively with the pentode, the triode used as anode bend detector and the diode, all the thermionic tubes being fed inductively. The apparent variability of the magnitude of the effect with the mode of current detection arises from the selectivity in response of the various detectors to different frequencies in the spectrum of the discharge current.

As has already been pointed out, the magnitude of the Joshi effect, determined with the crystal detectors, is very small. Thus e.g., the maximum observed with the Cambridge A.C. micro-ammeter is 13.3%, and with the Westinghouse instrument, 4.2%, both at 0.8 kV. With increasing  $V$ , the *effect* decreases and finally disappears, at 1.33 kV in the case of the former and at 1.2 kV with the latter. A crystal detector consists of a crystal in contact with a metal. The boundary between the crystal and the metal possesses a very high resistance, the value of which varies markedly with the direction of the impressed e.m.f., thus leading to rectification (Grondahl, *Rev. Mod. Phys.*, 1933, 5, 141; Wilson, "Semiconductors and Metals", Camb. Univ. Press, 1939). That the magnitude of  $\Delta i$  obtained with crystal detectors is small might, in part, be due to the appreciable resistance of the rectifier in the low-resistance direction, especially at small voltages applied across the instrument.

As compared with the crystal detectors, the magnitude of  $\Delta i$  observed with the vacuo-junction is considerable, the maximum being 23% at 0.67 kV. With increase in  $V$ ,  $\% \Delta i$  decreases and falls below 1.0 near about 2.8 kV. The net *effect*  $\Delta i$  is maximum at 0.8 kV, after which it decreases with  $V$ . According to Joshi (*Proc. Ind. Acad. Sci.*, 1945, A 22, 225), the vacuo-junctions have a stable characteristic over a wide range of applied  $V$  and frequency of the A.C. supply. For large currents or high frequencies, however, errors due to the 'skin effect' creep in. Further, since in this mode of current detection an appreciable resistance is introduced, a reduction of the H.F. oscillations occurs prior to irradiation. This would reduce  $\Delta i$ . In a thermal device like the vacuo-junction, reduction in  $\Delta i$  due to resistive damping of  $i_{HF}$  is, however, not appreciable, since the corresponding loss is represented by conversion into heat. Due to the stray capacity between the heater wire and the thermocouple, on the other hand, high frequencies may find their way into the thermocouple circuit and may consequently be lost.

The maximum  $\Delta i$  (28.3 % at 0.8 kV) obtained with the inductively fed diode is higher than that obtained with the vacuo-junction. This is to be anticipated in view of the low ohmic resistance in the oscillatory circuit. The net *effect*  $\Delta i$  is also maximum at 0.8 kV. With increase in  $V$  beyond 0.8 kV, both  $\Delta i$  and  $\% \Delta i$  decrease; their magnitudes become negligibly small near about 2.4 kV. The *effect* obtained with the diode, resistively coupled with the L. T. of the ozoniser, is small. The maximum photo-suppression observed is 6.4 % at 0.67 kV; at potentials higher than 0.93 kV, there is no photo-effect. That the magnitude of  $\Delta i$  is small is due to the fact that in this mode of current detection a high resistance is introduced in the oscillatory circuit; this increases the damping constant and also the 'skin effect', leading to a reduction of the H.F. oscillations prior to irradiation.

The triode used as an anode bend detector and coupled inductively with L. T. shows a  $\Delta i$  which is larger than that obtained with a diode coupled similarly; the maximum is 29.9 % at 0.8 kV (Table V). On the other hand,

$\% \Delta i$  observed with the triode used as a grid leak detector is small. Thus, with a leak resistance of  $5 \text{ M}\Omega$ ,  $\% \Delta i$  is maximum (21.2) at 0.67 kV; and decreases abruptly to 4.6 at 0.93 kV; with further rise in  $V$ , it decreases but slowly (Table V). Decreasing the leak resistance, whilst maintaining the capacitance constant, reduces the value of maximum  $\Delta i$ . Thus, with leaks of 5, 4, 3, 2 and  $1 \text{ M}\Omega$ , the maximum values of  $\% \Delta i$  observed are respectively 21.2, 18.2, 10.3, 13.7 and 10.7, all at 0.67 kV. The magnitude of  $\Delta i$  observed with the triode fed resistively is small.

The inductively fed pentode shows largest  $\Delta i$ , the maximum observed being 37.2 % at 0.8 kV. At higher  $V$ , both  $\Delta i$  and  $\% \Delta i$  decrease, but  $\% \Delta i$  in this case is appreciable even at 2.8 kV; at this potential other detectors show nil or negligible photo-suppression.

In the preliminary work on this effect in oxygen in these laboratories Cherian (*Proc. Indian Sci. Cong.*, 1942, Part III, *Chem. Sec.*, Abst. No. 56) who used a crystal detector observed a *positive effect*  $+ \Delta i$  at low  $V$ . A like phenomenon has been observed by the present author with thermionic tube detectors. Under identical conditions of excitation, the vacuo-junction, however, shows nil or the negative effect. When produced, the *positive effect* is large below  $V_m$ , at the point at which the current just begins to grow, decreases rapidly with  $V$ , and changes sign at potentials above  $V_m$ , after passing in many cases through a nul-point. Thus e.g., with the diode coupled inductively, a current gain of 1300% is observed at 0.59 kV. Increase of  $V$  to 0.61 kV reduces  $+ \Delta i$  to 16.7 %. At 0.64 kV, no change is observed in  $i$  under irradiation. With further increase in  $V$ , there occurs the negative effect, the magnitude of which increases to a maximum and then decreases. With the diode fed resistively,  $+ \Delta i$  is small, but decreases gradually with  $V$ ; further, it is distributed over a comparatively wide range of  $V$ . The observations with triode and pentode are generally similar to those with the diode coupled inductively.

The nature of potential variation of  $\Delta i$  and  $\% \Delta i$  is not, as is evident from the above, altered by a mere change in the mode of current detection. Thus, both  $\Delta i$  and  $\% \Delta i$  are maximum near 0.8 kV, after which they decrease with the applied  $V$ . This observation is in agreement with the general findings of Joshi (*Proc. Ind. Acad. Sci.*, 1945, A22, 389) that  $\% \Delta i$  is a maximum near  $V_m$ , and decreases thereafter with the applied  $V$ .

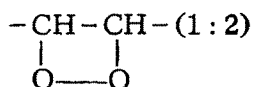
Grateful thanks of the author are due to Professor S. S. Joshi for having suggested the problem and for his keen interest in the work, and to Mr. G. S. Kamath, M. Sc., for his kind help in a part of the work.

# STUDIES ON THE MECHANISM OF AUTOXIDATION OF FATS. PART I KINETICS OF CATALYTIC OXIDATION OF OLEIC AND LINOLEIC ACIDS

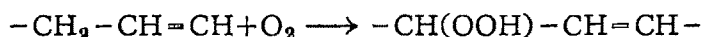
BY S. MUKHERJEE

The mechanism of autoxidation of unsaturated fatty acids by use of catalyst has been studied up to a primary stage of oxidation.

Although the autoxidation of fats and simple esters of unsaturated fatty acids have been the subject of a number of recent communications (Farion, *Chem. Ztg.*, 1904, 28, 1196; Goldschmidt *et al.*, *Ber.*, 1934, 67, 1588; Rieche, *Z. angew. Chem.*, 1937, 50, 520; Farmer and co-workers, *Trans. Faraday Soc.*, 1946, 42, 228; 1942, 38, 340; *J. Chem. Soc.*, 1943, 119; 1946, 10), it has not been possible to explain the primary process of autoxidation and to completely establish the nature of the products formed. Instead, the observations of the later investigators stand largely in contradiction to those of the earlier workers in the field, and as such the non-critical acceptance of any of these theories presents certain difficulties which must be clarified before arriving at a decision in favour of any of the hypotheses. The early theories which have been evolved with regard to autoxidation of fats have been founded on some concept concerning the initial addition of oxygen to the unsaturated linkage and the majority of workers have accepted the theory of formation of a heterocyclic peroxide of the formula (Farion, Goldschmidt, *loc. cit.*)



as the primary step in the autoxidation process. The existence of fatty acid peroxide containing such a configuration has been assumed on the basis of certain analytical data (viz. iodine and thiocyanogen value, peroxide, hydroxyl, carbonyl values, etc.) which have been interpreted as substantiating the existence of such a configuration in autoxidised unsaturated acids; but the more recent work of Farmer and co-workers (*loc. cit.*) has led to a considerable questioning concerning the validity of the cyclic peroxide theory. It appears to have been well established by Farmer that the autoxidation of all unconjugated olefinic compounds proceeds by addition of a molecule of oxygen to the carbon atom adjacent to the double bond to form a hydroperoxide having an intact double bond thus,



The most fundamental advance in the chemistry of autoxidation of fats was made by Farmer and Sutton when they isolated for the first time a moderately

pure peroxidised methyl oleate by molecular distillation of a partially oxidised sample of methyl oleate. It was further shown from spectrophotometric measurements that autoxidation of polyethenoid substances, whose double bonds are separated by methylenic groups, resulted in the formation of conjugated diene isomers (Farmer, Koch and Sutton, *J. Chem. Soc.*, 1943, 541; Bergstrom, *Arkiv Kemi Min. Geol.*, 1945, 14, Bd. 21A, 1). Further substantiation of the hydroperoxide theory was obtained when Atherton and Hilditch (*J. Chem. Soc.*, 1944, 105) isolated substantial proportion of suberic and octoic as well as azelaic and nonanoic acids, products predicted by Farmer as the fission products of hydroperoxido-oleic acid from the oxidative disruption of an autoxidised sample of oleic acid, thus proving to a large extent (though not necessarily exclusively) that peroxidation had occurred at the  $-\text{CH}_2-$  group adjacent to the ethenoid bond. However, on the basis of comparative studies of the autoxidation of methyl oleate and linoleate, Hilditch and co-workers (*ibid.*, 1945, 836; 1946, 1022; Hilditch, *J. Oil Col.-Chem. Assoc.*, 1947, 30, 1) disputed the concept that the attack by oxygen occurs only at the  $\alpha$ -methylenic positions. Hilditch has suggested a mechanism in which oxygen adds directly to the double bond, forming a transitory cyclic peroxide, which then rearranges to give hydroperoxides. But nevertheless, the isolation of the methyl hydroperoxido-oleate by Farmer appears to render the cycloperoxide theory of autoxidation untenable, and if we once accept the hydroperoxide theory, a reinterpretation of a considerable amount of previous experimental work becomes necessary and much of the speculation and conclusions concerning subsequent stages of autoxidation is vitiated.

Now, there are two major points of difference between the formulation as proposed by Hilditch and the  $\alpha$ -methylenic reactivity concept of Farmer *et al.* According to the former, a double bond shift must occur in all cases, even with a mono-olefines, if a hydroperoxide is the end product. The  $\alpha$ -methylenic concept, on the other hand, permits the formation of hydroperoxides with or without the shift of double bond from its original position. Another point of difference is that whereas the Farmer's postulation provides for the propagation of the chain reaction, no such mechanism is provided by the Hilditch's formulation. Then again, acceptance of Farmer's hydroperoxidation mechanism as the primary course of autoxidation apparently presents certain difficulties. Firstly, it must be borne in mind that any detachment of an  $\alpha$ -methylenic hydrogen atom from the olefin system to leave an active radical  $-\dot{\text{C}}\text{H} \cdot \text{CH}=\text{CH}-$  (the first likely stage in the production of an  $\alpha$ -methylenic  $-\text{OOH}$  group) will require the expenditure of 80 K. Cal. of energy which must be supplied from some not very obvious source; secondly, there exists numerous direct experimental evidences to show that conjugated compounds, including those in which the unsaturated centres are flanked by  $\alpha$ -methylenic groups, undergo peroxidation additively at the double bond systems, leaving the adjacent  $\alpha$ -methylenic group intact and iodine values of various olefinic substances including linoleates



(Paschke and Wheeler, *Oil & Soap*, 1944, 21, 52) have been found to fall during autoxidation to an extent that cannot be readily accounted for if it is assumed that all of the initial peroxides formed are hydroperoxides. For these reasons it has been considered of importance to make further studies on the mechanism of the autoxidation process to arrive at a more definite conclusion.

It may be stated that the complete understanding of the early stages of the autoxidation process has by no means been achieved and the two main points regarding which confusion still exists are (i) whether any cyclic (& polymeric) peroxides are formed and (ii) whether any appreciable amount of unconjugated diene hydroperoxides is formed. The data presented in the paper are not as clear cut as they might be, but these preliminary experiments reflect some light on the structure of the peroxides formed in the early stages of autoxidation of oleic and linoleic acids. A detailed study of the catalytic oxidation of the unsaturated acids, oleic and linoleic, has been carried out with special reference to peroxide formation and saturation of double bonds in direct relationship to the amount of oxygen absorbed.

It has been a common observation that if a sample of oleic or linoleic acid is shaken in a Warburg instrument, there is a gradual absorption of oxygen, and if aqueous KOH is placed in the inner cup, a fall in the manometer reading takes place. But the speed of the reaction is extremely slow such that it takes a week or so for a small quantity of the acid to be oxidised completely. The speed of the reaction can be highly increased by raising the temperature to 98°, but at this temperature it is very difficult to maintain the temperature of the bath rigorously constant owing to a large radiation losses. For this reason recourse was taken to a method similar to that of Banks (*J. Soc. Chem. Ind.*, 1944, 63, 8) used for the rapid testing of antioxidants for fats, where it was demonstrated that the presence of a mere trace of haematin (1/7000th mg.) was able to accelerate the oxygen absorption of aqueous suspensions of linoleic acid at ordinary temperature

## EXPERIMENTAL

*Preparation of the Substrates.*—In such studies as mechanism and kinetics of oxidation the purity of the substance plays a prominent part. Hence, attention was paid to the purification of the substrates (viz. oleic and linoleic) employed in these experiments

*Oleic Acid.*—The U. S. P. grade oleic acid (I. V. 89.0) was distilled at reduced pressure and the middle portion of the fraction distilling at 232°-234°/15 mm. was collected. This was subjected to a further distillation at 0.1 mm. when the fraction coming out at 153° was collected. The I. V. of this sample was 89.9, identical with the theoretical value.

*Linoleic Acid.*—The B. D. H. linoleic acid (I. V. 178.0, theoretical value 181.2) when subjected to a similar distillation in vacuum at 17 mm. (b.p. 224°) and again at 1mm. at 147°, yielded an acid with I V. 179.25. For further purification, the modern chromatographic adsorption separation method was taken recourse to. In applying chromatography to the preparation of pure linoleic acid in the present work, appropriate, reproducible and experimentally determined conditions have been employed to remove the complication introduced by the lack of visual means of differentiation between the adsorbed bands. The results of preliminary experiments indicated that the activity of adsorbent alumina was the most important factor. Brochmann's alumina (E. Merck) diluted with 4 times of its weight of inactivated alumina, prepared by the method of Fisk (*Paint Tech.*, 1945, 10, 85, 107), was found most suitable for the present work; as the use of pure Brochmann's alumina resulted in poor separation it was found necessary to make such a dilution, determined by a set of preliminary experiments. By trial experiments the quantity of developing and eluting solvents to remove the fraction of low I. V. was determined and the proportions used in the following experiment have been found to be quite satisfactory for the present work; 15 g. of linoleic acid, obtained by distillation in vacuum, as detailed above, were dissolved in 100 c.c. of petroleum ether (E. Merck) and adsorbed on a column of Brochmann's alumina using 1:4 dilution (100 g. in a tube of 7/8th inch dia.). The chromatogram was developed with 500 ml. of petroleum ether in course of one hour, which eluted a fraction of I V. 179.8. The pure linoleic acid fraction was obtained by rapidly eluting with 1500 c.c. of petroleum ether applying vacuum at the bottom, at the same time maintaining a positive pressure of CO<sub>2</sub> at the top. During the process of removing the solvent by distillation in vacuum, a slow stream of CO<sub>2</sub> was maintained throughout to prevent oxidation. The product obtained has an I. V. of 181.1. The acid can be taken as sufficiently pure for all practical purposes. The recovery of acid was 86%. By repeating this procedure of chromatographic separation a considerable amount of the pure acid was prepared and stored under CO<sub>2</sub>.

*Measurement of Oxygen Absorption.*—The fatty acid emulsions were prepared after the method of Banks (*loc. cit.*) and were used directly for estimation of oxygen absorption using haematine catalyst (0.2 c.c. of a solution containing 7 mg./100 c.c.). Oxygen absorption was measured in the Warburg manometric apparatus in a manner similar to that described by Johnston and Frey (*Ind. Eng. Chem., Anal. Ed.*, 1941, 13, 479). The flask containing 500 mg. of the acid in suspension was flushed with oxygen for 3 minutes and connected to the manometer and shaken for 15 minutes in the thermostat at 37°±0.1° after which the haematine solution was tipped off from the side bulb and oxygen absorption followed manometrically. With both the acids a static method was resorted to.

In Tables I and II are shown the c.c. of oxygen absorbed by oleic and linoleic acids respectively with time.

TABLE I

*Oxygen absorption in the catalytic oxidation of oleic acid at 37°.*

Time.	C.c. O <sub>2</sub> absorbed at N. T. P.			Time.	C.c. O <sub>2</sub> absorbed at N. T. P.		
	No. 1.	No. 2.	No. 3.		No. 1.	No. 2.	No. 3.
1 hr.	4.08	4.0	3.85	8 min.	15.0	15.0	14.98
2	5.0	5.0	4.85	9	15.5	15.5	15.4
3	8.10	7.95	7.85	10	16.05	16.0	16.0
4	10.0	9.92	9.85	11	17.5	17.3	17.45
5	12.9	12.90	12.85	24	20.0	19.92	19.85
6	12.95	13.0	12.98	35	25.0	24.8	24.85
7	14.0	14.0	13.99	48	30.0	29.3	29.75

TABLE II

*Oxygen absorption in the catalytic oxidation of linoleic acid at 37°.*

Time.	C.c. O <sub>2</sub> absorbed at N. T. P.				Time.	C.c. O <sub>2</sub> absorbed at N. T. P.			
	No. 1.	No. 2.	No. 3.	No. 4.		No. 1.	No. 2.	No. 3.	No. 4.
15 min.	2.00	2.00	2.00	2.00	120 min.	20.0	20.0	20.0	19.9
30	4.85	4.80	4.80	5.00	180	25.10	25.0	25.1	25.0
45	6.45	6.40	6.45	6.45	210	30.2	30.0	30.0	30.0
60	8.02	8.0	8.0	8.0	300	40.95	41.0	41.0	40.86
75	10.05	10.2	10.0	10.1	600	43.9	44.0	44.0	43.90
90	15.0	15.0	14.93	14.95	1200	46.0	46.1	46.0	46.0
105	17.8	17.5	17.5	17.46	1500	46.8	46.9	47.0	46.45

These results are shown graphically in Fig. 1.

At each stage of oxidation carried out with a number of flasks the oxidised fatty acids were recovered by extraction with ether - absolute alcohol mixture (4 : 1), the solvent removed under vacuum, and the peroxide and iodine value determinations were made in the usual way. In Tables III and IV are shown the relationship between iodine and peroxide values with oxygen absorption, all the results being expressed in percentages for easy comparison.

TABLE III

*Catalytic oxidation of oleic acid at 37°.*

Time.	%O <sub>2</sub> absorbed.	Proxide value (obs.).	% Peroxide formation on basis of O <sub>2</sub> consumn.	% Peroxide formation on wt. basis.	Iodine value (obs.)	% Iodine No.	Drop in I. V.	
							Obs.	Calc.
2 hours.	10	173	90	5.6	84.5	95	4.59	5.02
4	20	372	48	12.3	81.0	80	8.9	11.06
8	30	345.6	30	11.5	73.0	80	16.0	10.3
15	35	400	35	13.3	63	70	23.9	12.0
24	40	304	21.8	12.1	61.2	68	28.7	10.9
35	50	282	18.5	9.4	49.5	55	40.4	8.5
48	60	280	17.5	8.9	46.0	49	43.9	8.0

TABLE IV

*Catalytic oxidation of linoleic acid at 37°.*

Time.	% O <sub>2</sub> absor- bed.	Peroxide value (obs.)	% Peroxide formation on basis of O <sub>2</sub> consumn.	% Peroxide formation on wt. basis.	Iodine value (obs.)	% Iodi- ne No.	Drop in I. V.	
							Obs.	Calc.
0.5 hr.	10	1000	100	16	166.6	92.0	14.4	28.8
1.0	16	1650	100	27	166.3	86.7	24.2	48.6
1.25	20	2036	100	33.7	144.0	80.0	37.0	66.6
1.50	30	2985	98	49	129.6	72.0	51.4	88.2
1.75	35	5492	90	90	117.0	65.0	64.0	162.0
2.0	40	4550	70	80	95.4	52.0	85.6	144.0
3.0	50	3200	48	52.4	82.8	46.0	98.2	94.3
3.5	60	2750	40	45	72.6	40.0	108.4	81.0
4.0	80	2100	30	34.4	54.3	30.0	126.7	61.8

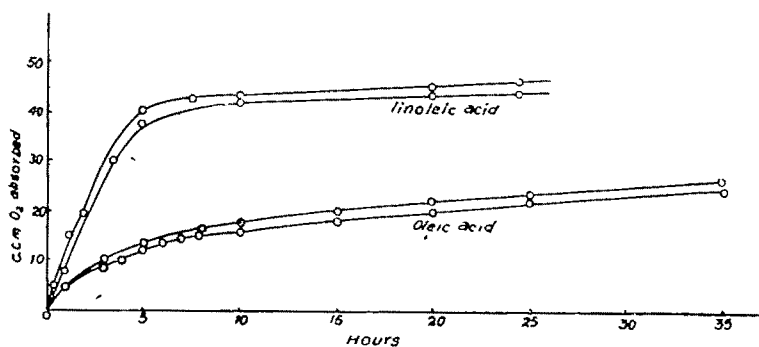
The figures in columns 4 and 7, viz. the percentage peroxide formation and iodine number are plotted against percentage oxygen absorption (column 2) in Figures 2 and 3.

In column 3 the peroxide values as determined experimentally are given; column 4 shows the theoretical peroxide value calculated on the basis of weight of oxygen absorbed, and on the assumption that peroxidation takes place entirely at the double bond; column 5 gives the percentages of peroxide formed calculated from the full theoretical peroxide value of 3050 and 6090. Column 7 gives the percentage iodine value, expressing the experimentally determined value as percentage of the theoretical iodine values, viz. 89.9 in case of oleic acid and 181.1 in case of linoleic acid, these being designated as 100%. Column 9 shows the drop in Iodine value calculated on the assumption that peroxide is formed at the double bond and its iodine value is nil.

## DISCUSSION

Figure 1 shows the oxygen absorption curves of the two fatty acids and it

FIG. 1



may be seen from the shape of the curve that in both the cases catalytic autoxi-

ation proceeds without any induction period, the velocity of autoxidation increasing with the double bond. In the presence of catalyst, the rate of absorption of oxygen is very vigorous at the beginning and falls off with time. It can also be observed that in no case even at the end of 48 hours the end-point in oxygen absorption is reached, although theoretically 100% oxygen has been consumed by the fat. The mechanism of oxidation of the two acids is discussed below.

*The Behaviour of Oleic Acid.*—From the results in Table III and the peroxide curve (Fig. 2) it can be observed that the absorbed oxygen is probably taken up only in the peroxide form at the initial stages, which corresponds to the oxygen absorption below 10%. The percentage peroxidation decreases afterwards and the curve becomes flatter in the later stages of oxidation. From the iodine number figures (columns 8 and 9), viz drop in iodine value observed and that calculated from full peroxidation of the double bonds, it is clear that at the initial stage up to 20% oxygen absorption the double bond disappears quantitatively (Fig. 2) during autoxidation. Later on, the double bond does not disappear in this proportion of  $O_2$  consumption which proceeds at a much enhanced rate than can be expected from saturation of double bond alone. The only logical conclusion is that oxygen apart from attacking the double bond probably also brings about further oxidation at some other place in the acid molecule, possibly of the reactive methylene group.

FIG. 2

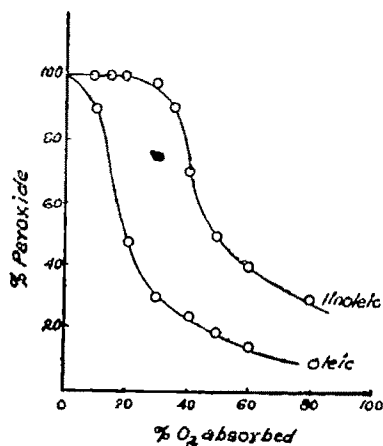
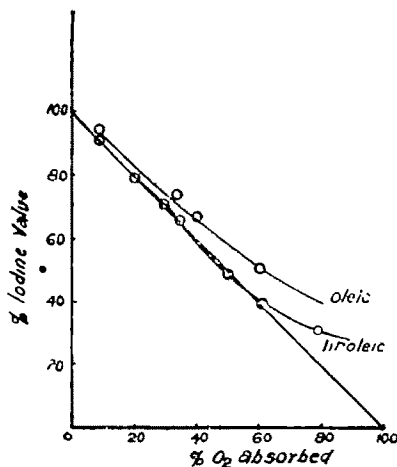


FIG. 3



*The Behaviour of Linoleic Acid.*—In the case of the more unsaturated linoleic acid, the absorbed oxygen can be seen to be utilised quantitatively in peroxidation of double bonds (Fig. 2) up to 35%, after which a sharp fall in peroxidation occurs and at 80% oxygen absorption, only one-third of the oxygen absorbed is used up in the formation of peroxides. The drop in the iodine value observed in this case is exactly half the theoretical value at the initial

stage where it can be seen from the peroxidation curve (Fig. 2), the oxygen is quantitatively used up in the peroxide formation. One can therefore at best conclude that for absorption of 1 molecule of oxygen only one double bond disappears. This relationship persists roughly up to 20% oxygen absorption (Table IV), after which the difference in the observed and calculated drop in iodine value is not very regular to arrive at a definite conclusion, though it may be sufficiently accurate to say from the intermediate position of the observed drop that further saturation of the other double bond proceeds at later stages in oxidation. But, it is clear from the iodine number curve (Fig. 3) that the rate of decrease of iodine number with oxygen absorption remains fairly constant far above the region of 100% peroxide formation (20%  $O_2$ -absorption) and this linear relationship is broken nearly at 50%  $O_2$ -absorption, indicating that an intensive oxidation proceeds simultaneously with the addition of one oxygen molecule at the double bond.

With both the oleic and linoleic acids, however, in the final stages of oxidation the observed drop in iodine value has been greater than the calculated value which apparently seems anomalous. But if one considers the corresponding peroxide curves showing quite appreciable break or inflexion, signifying considerable and abrupt decomposition of primary products in the course of oxidation, it will be logical to assume that the observed discrepancy is due to the disappearance of the double bonds by polymerisation or condensation reactions which accompanies decomposition reactions.

Thus far it can be concluded that during the initial stages of oxidation (catalytic) of the unsaturated fatty acids, the oxygen absorbed is used totally in peroxide formation, and that the peroxides are formed entirely at the double bond and with diethenoid compounds only one of the double bonds is saturated by oxygen with a considerable velocity resulting in the formation of peroxides. Indications have also been obtained during the period of intensive oxidation following the initial stage of full saturation of double bonds by peroxidation, of the probable oxidation at the active methylene group, such that the observed drop in iodine value is less than that can be expected from complete saturation of double bonds by the formation of cyclic peroxides, and further work is needed to find out the nature of the products of oxidation when enhanced oxidation is taking place.

The author is indebted to Prof. M. N. Goswami for his valuable suggestions in course of the work. His thanks are also due to the Lady Tata Memorial Trust for the award of a scholarship to carry out the investigation.

DEPARTMENT OF APPLIED CHEMISTRY,  
UNIVERSITY COLLEGE OF SCIENCE,  
CALCUTTA.

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STUDIES ON THE MECHANISM OF AUTOXIDATION OF FATS.  
PART II. OXIDATION OF METHYL OLEATE AND  
METHYL LINOLEATE

By S. MUKHERJEE

In course of autoxidation of fatty acids like oleic and linoleic and their methyl esters, oxygen achieves its effect by initiating its attack additively at the double bond of the unsaturated fatty acid molecules with the formation of cyclic peroxides. Oxidation is next found to proceed with the formation of hydroperoxides at a stage when initial cycloperoxidation of the unsaturated fatty acid molecules generates adequate energy to cause the disruption of an  $\alpha$ -methylene hydrogen atom adjacent to the double bond.

In the previous paper (this *Journal*, 1950, 27, 230) the mechanism of autoxidation of unsaturated fatty acids by use of catalyst has been studied up to a primary stage of oxidation. The work outlined in this section has been conducted to study quantitatively the non-catalytic peroxidation and saturation of double bond relationship in a manner similar to that described in the previous paper using methyl oleate and linoleate as substrate. The oxidation was carried out at 37°, 60° and 110° with methyl oleate and at 37° only with the linoleate.

EXPERIMENTAL

The esters were prepared from the pure acids obtained as before by esterification with methyl alcohol by use of HCl gas as the catalyst. The esters were finally distilled under vacuum at 5 mm. to obtain pure products (b. p. 186° and 182.5° respectively). The autoxidation was carried out in 500 c.c. round-bottomed flasks by passing a slow stream of air from a compressor through the ester sufficient to keep the whole mass in a state of constant agitation. No mechanical shaking arrangement was provided. In experiments above the room temperature the flasks were immersed in an oil-bath, the temperature of which was regulated to maintain the esters at the desired temperature; usually a lower temperature (5°–8°) of the bath was required due to the exothermic nature of the reaction. At regular intervals a portion of the autoxidised sample was taken out and preserved in a refrigerator under CO<sub>2</sub> for subsequent analysis of peroxide, iodine and other values. The following tables represent the analytical figures obtained.

TABLE I

*Oxidation of methyl oleate at 37°.*

Days of blowing.	Peroxide values.	% Peroxide.*	Iodine value.	Drop in iodine value	
				Obs.	Calc.*†
0	0	—	89.9	—	—
2	100	3.3	87.0	2.9	2.90
4	125	4.1	86.2	3.7	3.71
6	150	4.7	85.7	4.2	4.30
14	250	8.2	83.5	6.4	7.4
21	325	10.6	82.9	7.0	9.5
28	350	17.7	81.8	8.1	10.5
31	450	15.0	80.9	9.0	13.5
35	500	16.8	79.5	10.4	14.9
37	555	18.2	78.0	11.9	16.4
40	700	23.3	76.0	13.9	21.0
50	1000	33.3	72.6	17.3	29.5

TABLE II

*Oxidation of methyl oleate at 60°.*

Days of blowing.	Peroxide value.	% Peroxide.*	Iodine value.	Drop in iodine value	
				Obs.	Calc.**
0	0	—	89.9	—	—
3	400	13.3	78.8	11.3	11.9
7	810	26.7	77.4	12.5	23.8
14	1200	40.0	61.8	28.1	35.9
21	2710	90.0	36.5	53.4	80.9
28	1750	58.0	17.0	72.9	41.4

TABLE III

*Oxidation of methyl oleate at 100°.*

Hours of blowing.	Peroxide value.	% Peroxide.*	Iodine value.	Drop in iodine value	
				Obs.	Calc.**
4.5	687	22.6	69.5	20.4	20.3
24	1537	50.6	52.7	37.2	45.5
50	825	21.5	46.0	43.9	18.6
100	325	10.6	29.1	60.8	9.2

TABLE IV

*Oxidation of methyl linoleate at 37°.*

Hours of blowing.	Peroxide value.*	% Peroxide.*	Iodine value.	Drop in iodine value	% Diene conjugation.	
				Obs.	Calc.**	
5	50	0.84	172.3	0.90	1.90	0.0
50	250	4.1	112.0	61.2	7.25	6.2
100	1375	22.5	85.7	87.5	40.80	18.7
150	2300	37.7	67.9	106.3	68.30	25.5
192	1310	21.5	67.8	106.4	38.90	15.2

These results are shown graphically in Figures 1 and 2.

\* Calculated from full theor. p. v.

\*\* Calculated on assumption that O<sub>2</sub> adds to double bond.



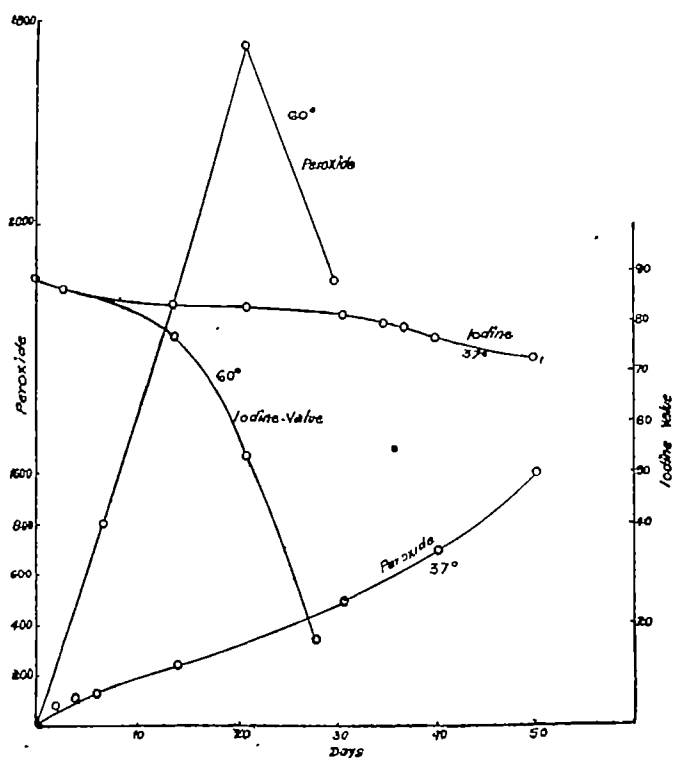
## DISCUSSION

*Methyl Oleate*

The formation of peroxides and drop in iodine number at the early stages of oxidation clearly indicate that peroxide formation takes place entirely at the double bond. Thus, at 37° (Table I), up to 5-6% peroxidation of the molecules, the observed and calculated drops are identical. This effect is exceedingly marked at 100° where rapid peroxidation up to a very high figure (viz. 20-22%) is entirely through saturation of the double bonds. But it can be observed, as the oxidation proceeds further, that drop in iodine value observed is definitely less than that can be expected from the peroxidation at the double bond only, but at the same time the value appears to be greater than that demanded by exclusive formation of hydroperoxide. This relationship of an

FIG. 1

*Oxidation of methyl oleate at 37° and at 60°.*



observed fall, lower than that calculated from the peroxide formation, persists throughout the oxidation of methyl oleate at 37°, and as the temperature is raised to 60°, the same relationship is seen to hold good except that towards

the end of the oxidation the disappearance of the double bond is rapid and is in fact greater than that can be calculated from the percentage peroxidation data. There has also taken place simultaneous decomposition of peroxides (vide Table I) along with a rapid fall in iodine number, which is probably an indication that various decomposition and secondary reactions might be taking place. At 100° the oxidation is extremely rapid, about 25% peroxidation taking place in course of 5 hours, the peroxide formation and disappearance of double bond relationship still persist, though progressively weakened as oxidation proceeds, and there the decomposition of peroxides plays the predominant role.

Now at 37°, as the depression is less than that can be expected from the percentage peroxide formation data, once the initial stage of cent per cent saturation of double bonds is passed, one may assume that oxidation proceeds at some other point, and most possibly at the reactive methylene group, so that the rate of disappearance of double bonds by peroxidation is counterbalanced or depressed due to the formation of some compounds, definitely peroxidic in nature (because of the still increasing peroxidation observed), which also contains in tact double bonds, thus accounting for the partial fall in iodine value.

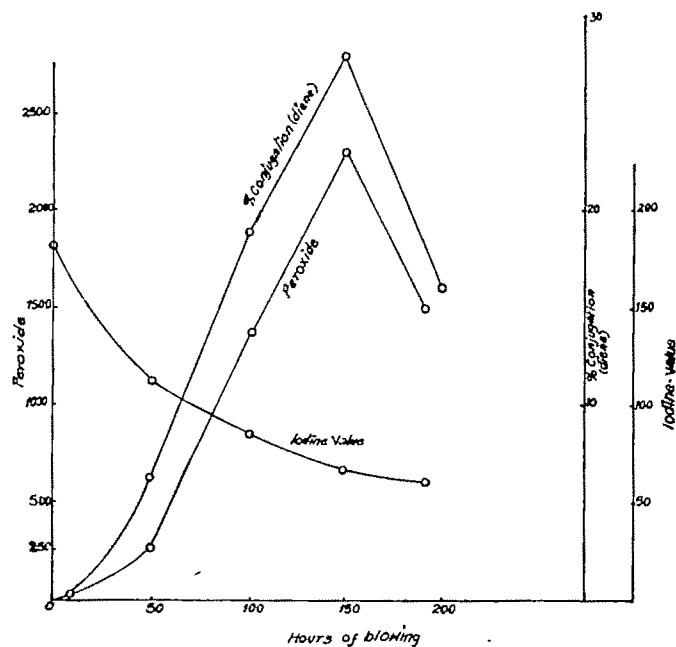
It evidently appears that hydroperoxidation of methyl oleate actually takes place, but Farmer's conclusions need certain modifications in the light of the above discussion and experimental results. He asserts that the primary product of peroxidation is a hydroperoxide. All the analytical data observed go to contradict this view and the opinion of the present author is that initial attack of oxygen is definitely at the ethenoid linkage as envisaged by early experimenters. As the rate of oxidation rapidly increases with time, the oxygen is able to utilise part of the energy liberated in such drastic oxidation in bringing about the disruption of one H atom of the active methylene group, ultimately resulting in the formation of compounds of hydroperoxidic nature. Moreover, it is very difficult to explain the formation of hydroperoxide at the initial stage because of the fact that separation of an  $\alpha$ -methylenic hydrogen atom requires 80 K. Cal. of energy, which must be supplied in some form or other, if hydroperoxidation starts at the beginning, and, hence the view expressed by the present author stands in a better position if at the same time it is remembered that the oxidation of methyl oleate is an exothermic reaction, and the heat evolved at the initial stage of cycloperoxidation might be sufficient to supply the energy requirement for subsequent hydroperoxidation of the methyl oleate.

#### *The Oxidation of Methyl Linoleate*

The conjugated diene unsaturation produced during the oxidation of methyl linoleate and recorded in Table IV above has been determined from the extinction coefficient of the absorption bands at 232 m $\mu$  (Brice *et al.*, *Oil & Soap*, 1945, 22,219). For this purpose solutions of the autoxidised esters

in absolute alcohol were employed. The ultraviolet spectra were obtained by means of a quartz spectrograph equipped with a Spekker photometer and a condensed tungsten-steel spark source of light. The maximum optical densities ( $\log_{10} I_0/I$ ) at 2320 Å were determined by visual examination and interpolation of the match points on Kodak B20 plates. The photometer was carefully calibrated before each measurement by determination of blank match points, and the recording spectra were completed in each case within 15 minutes of admitting air to the specimen in order to prevent oxidation and polymerisation reactions.

FIG. 2  
*Oxidation of methyl linoleate.*



The oxidation of methyl linoleate proceeds with a very short induction period, the peroxide values steadily rising to a certain maximum, followed by a rapid decomposition. The peroxidation is accompanied by development of diene conjugation, the amount of the latter increasing with nearly equal speed with that of peroxides. In the early stages of oxidation, the observed fall in iodine value is nearly an exact half of that can be expected from the theoretically calculated value of complete saturation of both the double bonds indicating, as in the case of catalytic oxidation of linoleic acid, that peroxidation of only one of the two double bonds takes place. The observed drop in iodine value soon, however, surpasses that calculated on the latter assumption. This can be explained by consideration of the progressive failure of the peroxide values

to indicate the absolute total quantity of peroxides produced in consequence of the secondary changes of the same, together with the presence of increasingly significant proportions of diene conjugation, which considerably vitiates the iodine value determination as carried out by Wij's method. It may be noticed that so long the saturation of one of the double bonds proceeds, there appears no significant amount of diene conjugation. From the data accumulated in this paper, it can be concluded that

(1) Oxidation of methyl linoleate starts by saturation of one of the double bonds only up to a certain initial stage of slow oxidation.

(2) Once this stage is passed, drastic oxidation results in simultaneous oxidation of the reactive methylene group of the acid molecule giving a hydroperoxide which afterwards rearranges with the formation of conjugated diene compounds, capable of further transformations such as polymerisation and decomposition. Any hypothesis of the initial formation of hydroperoxides, as postulated by Farmer, cannot be justified from the results obtained in course of the present investigation.

*Development of Hydroxyl groups in the Oxidation of Methyl  
Oleate and Linoleate*

The estimation of hydroxyl number of the oxidised samples described in Tables I, II and III has been carried out by the rapid method of Roberts and Schuette (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 287) by heating in sealed tubes with acetic anhydride and the results are shown in the following tables.

TABLE V

*Development of OH groups in the oxidation of methyl oleate*  
(cf. Table II)

Experiments.	Acetyl No.	Peroxide value,
1. Methyl oleate oxidised at 100° for 4.5 hours	0.0	687
2. Methyl oleate " " 100° " 24 "	22.8	1537
3. Methyl oleate " " 100° " 50 "	33.9	825
4. Methyl oleate " " 100° " 100 "	23.75	325
5. Methyl oleate " " 37° " 50 days	38.0	—

TABLE VI

*Development of OH groups in the oxidation of methyl linoleate*  
(cf. Table IV)

Experiments.	Acetyl No.	Peroxide value
1. Methyl linoleate oxidised for 5 hrs. at 37°	0.02	50
2. Methyl linoleate " " 50 " " 37°	27.51	200
3. Methyl linoleate " " 100 " " 37°	51.51	1375
4. Methyl linoleate " " 150 " " 37°	83.03	2300
5. Methyl linoleate " " 191 " " 37°	77.75	1610

The results in Tables V and VI tend to show that development of hydroxyl groups during the oxidation of methyl oleate or linoleate takes place after an initial stage of full saturation of the double bonds by peroxidation alone, as practically very little hydroxyl groups have been introduced at the end of  $4\frac{1}{2}$  hours in case of methyl oleate at  $100^{\circ}$ , and 5 hours in case of methyl linoleate at  $37^{\circ}$  where it can be seen from the peroxide figures (Tables II and IV) that cent per cent peroxidation of the double bonds takes place. This indicates that hydroxyl compounds are derived possibly from the products of decomposition of the primary peroxides or more likely, the hydroperoxides which are formed subsequently. It may also be observed that with methyl linoleate the development of hydroxyl group increases *pro passu* up to a certain stage after which a fall in peroxide concentration is also accompanied by a decrease in the acetyl number.

The experimental evidences that have been obtained so far go to support the view that in course of the oxidation of oleic and linoleic acids and their methyl esters, the primary point of attack is the ethenoid bond of the unsaturated fatty acid molecules, entirely with the formation of peroxides. With the diethenoid linoleic acids, it has been established that during the initial stage of peroxidation only one of the two double bonds is saturated by oxygen in considerable speed. In the later stages of oxidation, however, both in the case of mono- and di-unsaturated acid, the oxygen further attacks the molecules possibly at the active methylene group with the formation of compounds, hydroperoxidic in nature. Since the separation of an  $\alpha$ -methylenic hydrogen atom requires about 80 K. Cal. of energy, any hypothesis of initial hydroperoxidation seems to be impossible. The present investigation suggests that during the early stages of oxidation a gradual activation of the fat molecules proceeds and active fat peroxides are being formed; accumulation of these and greatly accelerated rate of oxygen absorption may therefore result in facilitating the acquisition of a sufficient critical increment of energy by the fat molecules such that hydroperoxidation of the reactive methylene groups by separation of one  $\alpha$ -methylenic H atoms proceeds during the second phase of oxidation reactions. This investigation thus establishes the old peroxide theory and at the same time adds substantial support to the modern hydroperoxidation mechanism of autoxidation of fats, thus harmonising the discrepancies raised by different workers.

The author is indebted to Prof. M. N. Goswami, Head of the Department of Applied Chemistry, Calcutta University for his valuable suggestions in course of the work. The author's thanks are also due to the Lady Tata Memorial Trust, Bombay for their kindly awarding a scholarship to carry out the investigation.

APPLIED CHEMISTRY DEPARTMENT,  
UNIVERSITY COLLEGE OF SCIENCE,  
CALCUTTA,

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## COLORIMETRIC ESTIMATION OF IRON WITH QUINALDINIC ACID. A CRITICAL STUDY

BY ANIL KUMAR MAJUMDAR AND BUDDHADRV SEN

The reagent quinaldinic acid has been utilised for the colorimetric estimation of iron visually from 0.4 p.p.m. to 130 p.p.m. and from 0.8 p.p.m. to 18 p.p.m. in a photoelectric colorimeter with a 20 mm. cell. The effect of various factors and of diverse ions on the coloured complex has been critically examined. The maximum absorption due to the coloured complex was found to be in the region of 515  $\mu$ .

The reagent quinaldinic acid was used by Ray and Bose (*Z. anal. Chem.*, 1933, 95, 400) for the estimation of copper, cadmium, zinc, etc. They further found that the reagent could also be utilised for the colorimetric determination of ferrous iron. The colour of complex formed deepens with excess of cyanide, and this forms the basis for the colorimetric estimation of iron.

The purpose of the present investigation is to find out whether this reagent quinaldinic acid, which is cheaper and very easily prepared, can be recommended for the colorimetric determination of iron. With this idea a critical study of the various factors which may affect the formation of the coloured complex, including a study of the effect of varying concentrations of diverse ions usually encountered in routine analysis, has been made.

The maximum absorption due to the coloured system is found to be in the region of 515  $\mu$ . Though cyanide intensifies the colour, the maximum absorption region is not shifted either in presence of a large excess of it or of the reagent. Reducing agents, such as, hydroxylamine hydrochloride, hydrazine sulphate and hydrogen sulphide, are found to have no influence on the region of maximum absorption. In a cell of thickness 20 mm. and in a volume of 25 c. c., iron present should not be more than 0.4 mg., but during visual observations with a colorimeter of the Duboscq type, the concentration of iron may be increased to 4 mg. in a volume of 30 c. c. and the minimum amount of iron that can be accurately estimated is 27 in a volume of 5 c. c.

The function of cyanide is to give necessary alkalinity, but it seems probable that the cyanide also enters into the composition of the coloured compound.

### EXPERIMENTAL

*Apparatus and Solutions.*—The optical density measurements were made with a Lumetron colorimeter of model 402 EF of Photovolt Corporation. Solutions for such measurements were taken in a corex glass cell of capacity 16 c. c. and of thickness 20 mm.

Chemicals used were all of the reagent quality. Standard solutions of iron were prepared from recrystallised Mohr salt (AnalaR) with water and a

few c.c. of concentrated  $\text{H}_2\text{SO}_4$ , and the iron content of each solution was determined volumetrically by permanganate. Solutions weaker than those were prepared by dilution with water which was previously boiled to remove dissolved oxygen.

A solution of sodium quinaldinate was made from 1 g. of quinaldinic acid (prepared according to the method of Hammick, *I. Chem. Soc.*, 1923, 123, 2882, and recrystallised) per 100 c.c. of the solution.

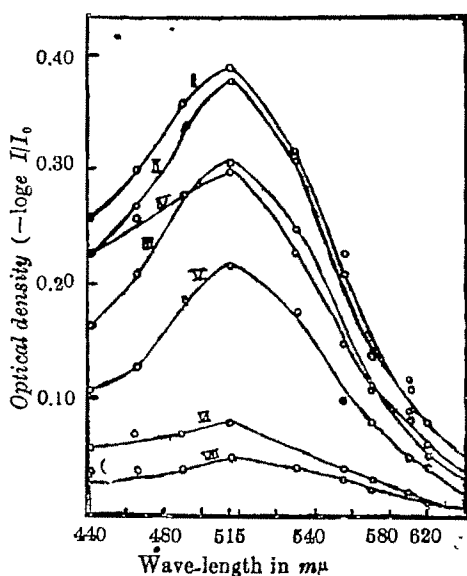
The effect of cyanide on the colour system was studied with a 2% solution of sodium cyanide, but in all other studies a 10% solution was used.

As reducing agents, a 5% solution of hydroxylamine hydrochloride, a 3% solution of hydrazine sulphate and a saturated solution of hydrogen sulphide at  $30^\circ$  were used.

Standard solutions of diverse ions were obtained from the nitrate or sulphate salts of cations and from the sodium or potassium salts of the anions. For studying the effect of mineral acids, 1% solutions of the acids were prepared.

**Colour Reaction.**—The reddish purple colour formed by the ferrous ion with the reagent showed maximum absorption in the region of  $515\text{ }\mu$ . When sodium cyanide was added, after the addition of the reagent, to the ferrous ion, the intensity of colour increased, but the maximum absorption region remained the same even when a large excess of cyanide was used. Varying amounts of iron and the reagent had also no influence on the region of maximum absorption. Reducing agents such as, hydroxylamine hydrochloride, hydrazine sulphate, hydrogen sulphide, etc., were found to be without any influence on the maximum absorption region (curves in Fig. 1 show the effect).

FIG. 1.



I. Fe 0.1 mg,  $\text{NH}_2\text{OH.HCl}$ , 50 mg., ( $\text{NH}_4\text{-NH}_4\text{H}_2\text{SO}_4$ , 30 mg) ; reagent 10 mg., NaCN, 100 mg.

II. Fe 0.1 mg., reagent 10 mg., NaCN, 100 mg.,  $\text{H}_2\text{S}$ -water, 4 c.c.

III. Fe 0.1 mg., reagent 10 mg., NaCN, 40 mg.

IV. Fe 0.2 mg., reagent 10 mg. (only in this case vol. of the soln. was made up with alcohol).

V. Fe 0.1 mg., reagent 1 mg., NaCN 40 mg.

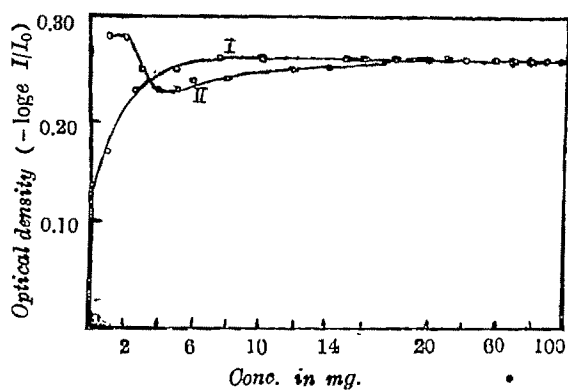
VI. Fe 0.04 mg., reagent 10 mg., NaCN, 20 mg.

VII. Fe 0.04 mg., reagent 0.4 mg., NaCN, 20 mg.

Ferrous ion forms with the reagent quinaldinic acid an inner metallic tetra-coordinated complex (Ray and Bose, *loc. cit.*). The increase in the intensity of the colour by the cyanide appears to be due to the formation of a hexa-co-ordinated complex of the type  $\text{Na}_2[\text{Fe}(\text{C}_{10}\text{H}_8\text{NO}_2)_2(\text{CN})_2]$ . The alkalinity caused by the alkali cyanide does not intensify the colour as the dilute solution of caustic soda or of sodium acetate has been found to decompose the complex with the precipitation of iron.

*Effect of the Reagent, Cyanide and of Reducing Agents.*—In order to study the effect of the different reagents on the coloured system at the wave-length of maximum absorption  $515 \mu$ , varying amounts of the reagent were added keeping the concentration of iron and cyanide constant in a volume of 25 c.c. The effect of cyanide was similarly studied in the region of  $515 \mu$ , with varying amounts of cyanide, while the concentrations of iron and the reagent were kept the same in the same volume of the solution. The results are graphically represented in curves I, II in Fig 2. In the same way the influence of the reducing agents, such as hydroxylamine hydrochloride, hydrazine sulphate, and

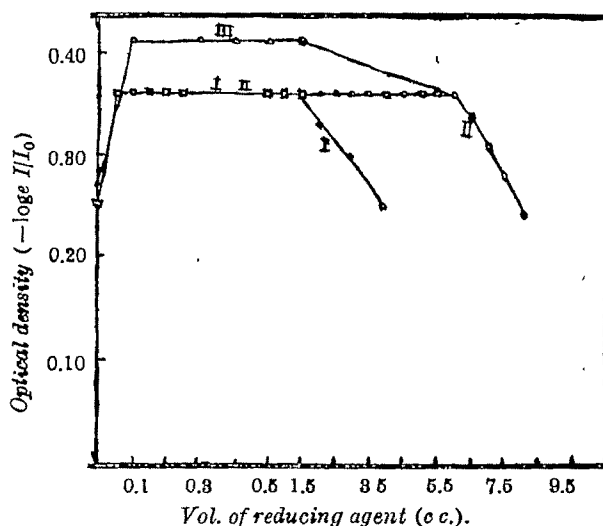
FIG. 2



(Soln. contains 0.1 mg. of Fe)

Curves I and II refer respectively to reagent and cyanide.

FIG. 3



(Soln. contains 0.1 mg. Fe and 10 mg. reagent)

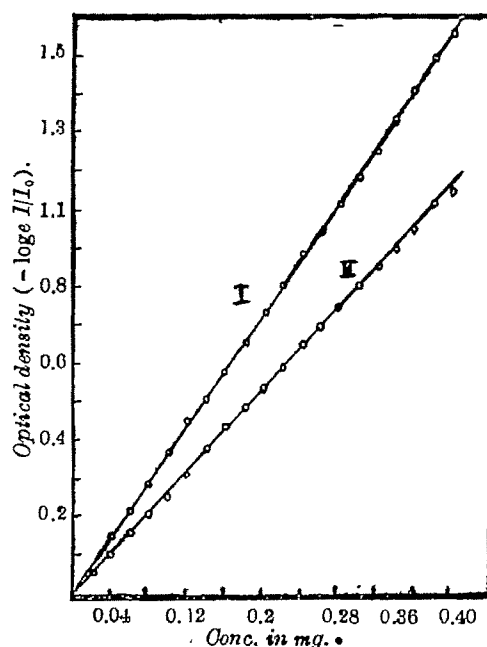
Curves I—III refer respectively to hydroxylamine hydrochloride, hydrazine sulphate and  $\text{H}_2\text{S}$ ,

hydrogen sulphide was investigated and the results represented in curves I-III in Fig.3. The curves show that for the maximum colour development the reagent and cyanide required are respectively about 50 and 360 times the amount of the iron present, and the reducing agent hydroxylamine hydrochloride may be tolerated up to 750 times and the hydrazine sulphate up to 1800 times the amount of iron without affecting the absorption.



That Beer's law is obeyed by the colour system is shown by the fact that straight lines are obtained when the optical densities at  $515\text{ }\mu$ , for a number of solutions containing iron from  $2 \times 10^{-5}\text{ g.}$  to  $4 \times 10^{-4}\text{ g.}$  are plotted against the respective concentrations (Fig. 4). The procedure followed was to add with stirring to the ferrous iron solution solutions of hydroxylamine hydrochloride or hydrazine sulphate, the reagent and the sodium cyanide, in the order as stated, and the volume of the solution was made up to 25 c.c. with water. The optical density of the solution thus obtained was measured. A few determinations were also made without the addition of the reducing agents. When the amount of iron is more than 0.4 mg in 25 c.c. solution, the transmittancy is very small and hence measurements in that region have been avoided.

FIG. 4



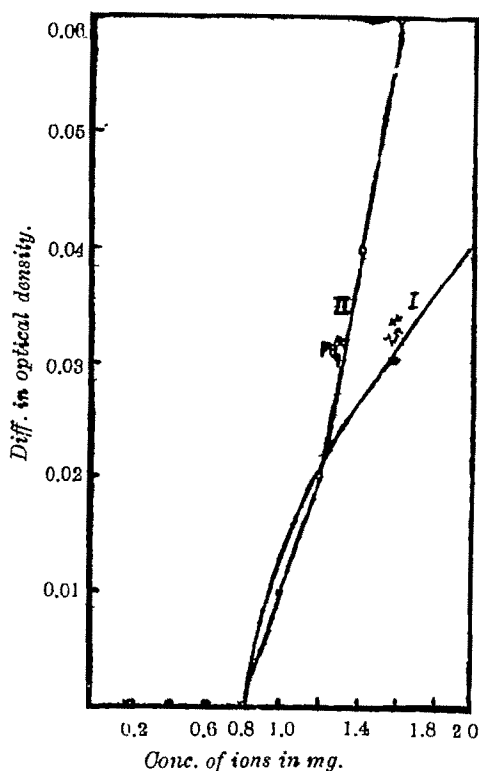
- I. With reducing agent (hydroxylamine hydrochloride or hydrazine sulphate).  
 II. Without reducing agent.

Some determinations were made by visual comparison in Klett's bio-colorimeter and the results obtained are given in Table I. The colour system was found to obey Beer's law through a long range of concentration studied up to 4 mg. in a volume of 30 c.c. Procedure followed was exactly the same as with the photo-electric colorimeter. The minimum amount of iron that can be estimated with accuracy is 27 in a volume of 5 c.c. If the iron concentration is over 4 mg., the colour developed in a volume of 30 c.c. is too intense for visual comparison.



was to be determined and then hydroxylamine hydrochloride (1 c.c.), the reagent (1 c.c.) and the cyanide (1 c.c.) in the order stated and the volume was made up to 25 c.c. (cf. Figs. 5-7). With the increase in the concentration of cyanide the effect due to other ions remained the same but those due to mineral acids decreased.

FIG. 7.



The following ions interfere when present at a concentration of in 25 c.c. :—  
 $\text{Ni}^{++}$  4 mg.,  $\text{Mn}^{++}$  4 mg.,  $\text{Cd}^{++}$  13 mg.,  $\text{Zn}^{++}$  0.9 mg.,  $\text{Pb}^{++}$  10 mg.,  $\text{PO}_4^{--}$ ,  
 0.9 mg.,  $\text{F}^-$  4 mg., citrate 0.3 mg.,  $\text{C}_4\text{H}_4\text{O}_6$  0.4 mg.,  $\text{HNO}_3$  40 mg.,  
 $\text{H}_2\text{SO}_4$  70 mg.,  $\text{HCl}$ , 80 mg.

The following ions are without any effect even at a concentration of 100 mg. in 25 c. c. :— $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{SO}_4^{--}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ .

Traces of copper or oxalate have a marked interfering effect.

PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF COMPLEX  
METALLIC FERRO AND FERRICYANIDES. PART X. STUDIES  
ON THE ADSORPTION OF  $\text{Cu}^{++}$  AND  $\text{FeCy}_6^{+++}$  IONS BY  
COPPER FERROCYANIDE SOL, AND THE EFFECT OF  
DILUTION ON THE COMPOSITION OF COPPER  
FERROCYANIDE

BY HARISH C. GAUR AND ABANI K. BHATTACHARYA

Composition of the copper ferrocyanide sol has been studied from the adsorption of  $\text{Cu}^{++}$  and  $\text{FeCy}_6^{+++}$  ions. Influence of hydrolysis and adsorption on the composition of the compound has been confirmed.

In continuation of the physico-chemical studies on the composition of copper ferrocyanide (Bhattacharya and Gaur, this *Journal*, 1947, 24, 487, 499 ; 1948, 25, 27) the adsorption of  $\text{Cu}^{++}$  and  $\text{FeCy}_6^{+++}$  ions by copper ferrocyanide sol, and also the effect of dilution on the sol have been studied, in order to throw further light on the composition and behaviour of copper ferrocyanide. Influence of hydrolysis and adsorption on the composition of the compound has been confirmed by experimental results.

EXPERIMENTAL

*Adsorption Experiments.*—Copper ferrocyanide sol (25 g./litre) was prepared by mixing copper sulphate and potassium ferrocyanide solutions in the molar ratio of 1 : 1. The sols prepared in other ratios were unstable, and so were the sols of higher concentrations.

For carrying out the adsorption experiments, the sols were dialysed for 7 to 8 days when the amount of free  $\text{FeCy}_6^{+++}$  in the dialysate was almost negligible. In order to study the adsorption of  $\text{FeCy}_6^{+++}$ , 50 c.c. of the dialysed sol were taken and mixed with equal volumes of  $M/20$ ,  $M/25$ ,  $M/40$ ,  $M/50$ ,  $M/80$ ,  $M/100$  potassium ferrocyanide solutions in different glass cylinders. In each case the contents were mixed up well, and coagulated by addition of A. R. ammonium sulphate, and the equilibrium concentration of potassium ferrocyanide was determined volumetrically by titrating against standardised solution of potassium permanganate. A blank reading with 50 c. c. of the sol, and an equal volume of water was also taken, and the readings in other cases were corrected for this ferrocyanide, which was originally present in the sol for its stability. From the initial and equilibrium concentrations of potassium ferrocyanide, the amount of  $\text{K}_4\text{FeCy}_6$  adsorbed per g. of the complex was calculated. The adsorption of  $\text{Cu}^{++}$  ions was carried out in a similar way.  $\text{Cu}^{++}$  was estimated by iodometry.

TABLE I

*Adsorption of  $\text{Cu}^{++}$  by copper ferrocyanide sol.*

( cf. Fig. 1 )

Conc. of $\text{CuSO}_4$ added (after correcting for stabilising $\text{FeCy}_6'''$ )	Equilib. conc.	$\text{CuSO}_4$ adsorbed per g. of the complex. (x/m)
1 7.781 g./litre	7.122 g./litre	1.01 m. moles
2 6.309	5.806	1.48
3 3.814	3.332	1.21
4 2.956	2.554	1.01
5 2.4767	2.120	0.85

FIG. 1

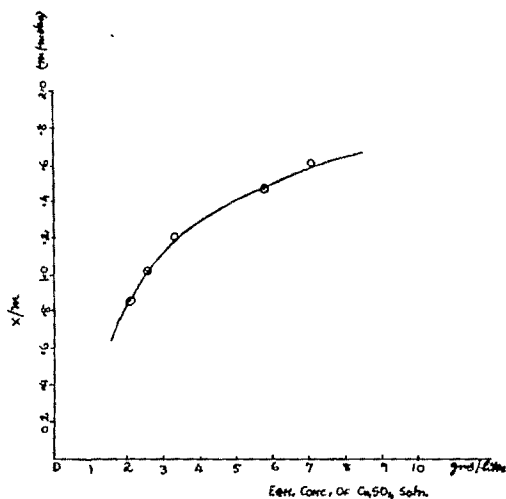
*Adsorption of  $\text{Cu}^{++}$  by copper  
ferrocyanide sol.*

FIG. 2

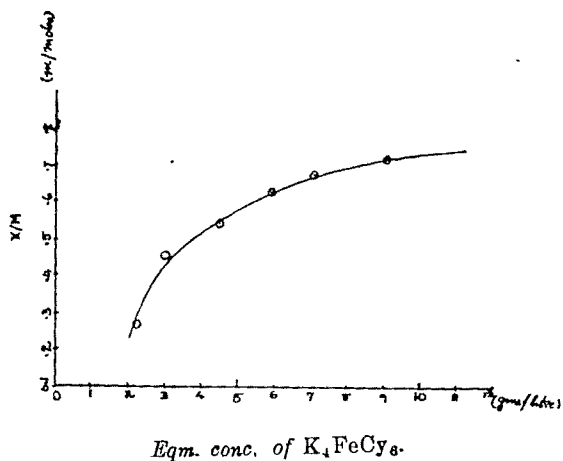
*Adsorption of  $\text{FeCy}_6'''$  by  
copper ferrocyanide sol.*

TABLE II

*Adsorption of  $\text{FeCy}_6'''$  by copper ferrocyanide sol.*

( cf. Fig. 2 )

Conc. of $\text{K}_4\text{FeCy}_6$ (after correcting for the stabilising $\text{FeCy}_6'''$ )	Equilib conc	$\text{K}_4\text{FeCy}_6$ absorbed per g. of the complex.
1 18.8938 g./litre	18.322 g./litre	0.82 m. moles
2 14.8395	14.3082	0.58
3 12.4485	11.9697	0.52
4 9.4655	9.0802	0.44
5 5.3345	6.0033	0.36
6 4.7145	4.5523	0.17

*Effect of Dilution on the Sol.*—Samples of the sols dialysed for 1, 2, 3, 4, and 5 days were prepared, the volume in each case was made the same so that the concentration of the sol in each case was 2.5 g./litre of the complex. The undialysed and the dialysed sols were diluted, and  $\text{FeCy}_6^{'''}$  released by the original, and twice, thrice, and four times diluted sols on coagulation was determined by titrating against standard potassium permanganate. The concentration of released  $\text{FeCy}_6^{'''}$  was so low that the usual method of deHaën for its estimation by titrating against very dilute potassium permanganate was found to be unreliable. The end-point was detected by adding excess of  $N/400$  potassium permanganate, and back titrating the residual excess against  $N/400$  potassium ferrocyanide, potentiometrically. A bright platinum foil was used as an indicator electrode, in conjunction with a saturated calomel electrode. The end-point was detected by a sudden fall in the value of  $dE/dC$  and it was very sharp. The amount of  $\text{FeCy}_6^{''}$  released per g. of the complex was calculated as  $\text{K}_4\text{FeCy}_6$ . Results are given below.

TABLE III  
*Copper ferrocyanide sol (1:1)*  
( Strength = 2.5 g./litre )  
( cf. Fig. 3 )

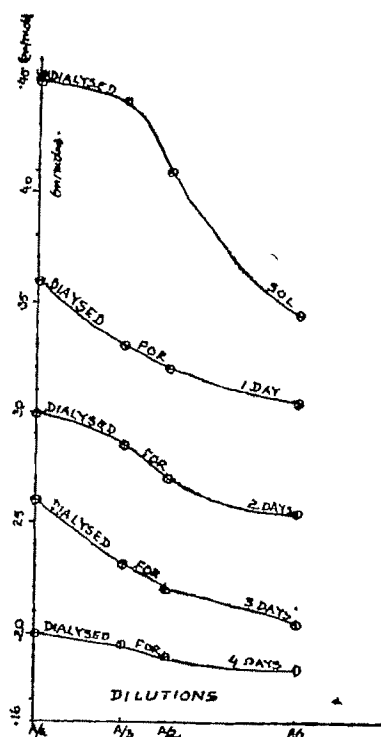
Conc. of the sol.	Equiv. vol. of $N/400$ $\text{K}_4\text{FeCy}_6$ for 20 c.c. of supernatant layer.	$\text{K}_4\text{FeCy}_6$ per litre of the supernatant layer (m./moles)	$\text{K}_4\text{FeCy}_6$ released per g. of the sol. (m./moles)
Undialysed sol.			
A/1	7.3 c.c.	$9.125 \times 10^{-1}$	0.345
A/2	4.1	5.125	0.410
A/3	2.95	3.689	0.442
A/4	2.25	2.812	0.450
Sol dialysed for 1 day.			
A/1	6.1	7.625	0.305
A/2	3.2	4.00	0.32
A/3	2.2	2.75	0.33
A/4	1.8	2.25	0.36
Sol dialysed for 2 days.			
A/1	5.1	6.375	0.255
A/2	2.7	3.375	0.270
A/3	1.9	2.375	0.285
A/4	1.5	1.812	0.300
Sol dialysed for 3 days.			
A/1	4.1	5.125	0.205
A/2	2.2	2.750	0.220
A/3	1.55	1.938	0.232
A/4	1.30	1.625	0.260
Sol dialysed for 4 days.			
A/1	3.7	4.625	0.185
A/2	1.9	2.375	0.190
A/3	1.3	1.625	0.195
A/4	1.0	1.250	0.200

## DISCUSSION

The accompanying curves (Fig. 3) show that the release of  $\text{FeCy}_6'''$  per g. of the complex is much greater in the undialysed sol. The proportional increase of  $\text{FeCy}_6'''$  on dilution is also greater in the undialysed sol than when dialysed. Gradual release of  $\text{FeCy}_6'''$  on dilution suggests that the sol suffers hydrolysis to some extent, as otherwise the concentration of the released  $\text{FeCy}_6'''$  per g. on dilution and precipitation of the sol would have been almost constant.

FIG. 3

*Effect of dilution on copper ferrocyanide sol.*



In the study of the composition of copper ferrocyanide by physico-chemical methods (Bhattacharya and Gaur, this *Journal*, 1947, 24, 487, 499; 1948, 25, 27) it was observed by us that the composition of the complex suffered a change from its normal formula due to combined effects of hydrolysis and adsorption. The observations of adsorption of  $\text{Cu}^{++}$  and  $\text{FeCy}_6'''$  ions by copper ferrocyanide sol and also its effect of dilution support the view advanced by us.

## STUDIES ON 'LIPASE' FROM OIL SEEDS. PART I. GENERAL STUDY OF THE RICINUS LIPASE FROM CASTOR SEEDS

BY G. V. NEVGI AND C. V. RAMAKRISHNAN

The effect of different factors like the nature of the buffer, the effect of concentration of the buffer, substrate and enzyme on the activity of ricinus lipase from castor seed has been studied. An attempt has been made to prepare lipase which keeps its activity fairly constant for an appreciably long time.

Reynolds Green ( *Proc. Roy. Soc.*, 1890, B, 48, 370 ) discovered the enzyme, Ricinus lipase ( *Ricinus communis* ) present in the castor seed. Willstätter and Waldschmidt ( *Z. physiol. Chem.*, 1923-24, 134, 161 ) found that the optimum  $p_H$  for the ricinus lipase from castor seed was between 4.7 and 5.0, varying slightly according to the buffer used. Tanaka (Eighth Int. Congress of Applied Chemistry, 1912, Sec. Vd, 11, 37; *J. Soc. Chem. Ind.*, 1912, 31, 884) prepared the lipase powder from castor seed. Longnecker and Haly ( *J. Amer. Chem. Soc.*, 1935, 57, 2019 ) modified Tanaka's method and prepared an active lipase powder.

As it is felt that 'lipase' can be used as a hydrolysing agent to hydrolyse oils in the soap industry as well as a synthetic agent to prepare synthetic fat, a detailed survey was undertaken to study the different oil seeds available in India for their lipolytic activity and the feasibility of obtaining a cheap and active lipase on a large scale. First of all, the lipolytic activity of castor seed was studied in detail.

### EXPERIMENTAL

The lipase powder was prepared from fresh "well ripened castor seeds" by Longnecker and Haly's method ( *loc. cit.* ). The fine powder obtained was preserved in a bottle after adding few drops of toluene to prevent bacterial action and used for the present work.

The different factors which control the activity of the lipase have been investigated by studying the hydrolysis of olive oil by ricinus lipase from castor seeds under different conditions.

*Effect of the Nature of the Buffer on the Optimum  $p_H$  of the Ricinus Lipase.*  
—Disodium phosphate-citric acid buffer mixtures of different  $p_H$  were prepared according to McIlvaine's method ( *J. Biol. Chem.*, 1921, 49, 183 ) and sodium acetate-hydrochloric acid and sodium acetate-acetic acid buffer mixtures of different  $p_H$  according to Walpole's method ( *J. Chem. Soc.*, 1914, 105, 2501, 2521 ).



The hydrolysis of olive oil by ricinus lipase was carried out at different  $p_H$  using different buffer mixtures.

Each set of experiments consisted of olive oil (1 c. c.), water (2 c. c.), lipase (.0.1 g.), and 5 c. c. of buffer of varying  $p_H$  value and a few drops of toluene in a conical flask. It was corked well and incubated for 24 hours at  $37^\circ$ . Always a blank accompanied each sample. Necessary precautions were taken to note readings under sterile conditions. After the period of incubation, each flask was taken out and the contents titrated against  $N/10$  sodium hydroxide. The difference between the sample and the blank gave the activity of the lipase in terms of c.c. of  $N/10$  sodium hydroxide. The results are given in the following tables.

TABLE I

*Optimum  $p_H$  for lipase using disodium phosphate-citric acid buffer.*

Set No.	Oil.	$p_H$ .	$N/10$ -s o d i u m h y d r o x i d e f o r		
			Sample.	Blank.	Free acid.
1	1.0 c.c.	2.4	19.0 c.c.	15.9 c.c.	3.1 c.c.
2	1.0	2.8	18.8	14.0	4.8
3	1.0	3.1	15.5	10.6	4.9
4	1.0	4.8	10.2	5.2	5.0
5	1.0	5.2	4.9	4.2	0.7
6	1.0	5.5	3.8	3.3	0.5
7	1.0	5.7	7.1	6.1	1.0
8	1.0	6.2	9.2	9.0	0.2

TABLE II

*Optimum  $p_H$  for lipase using sodium acetate-hydrochloric acid buffer.*

Set No.	Oil.	$p_H$ .	$N/10$ -s o d i u m h y d r o x i d e f o r		
			Sample.	Blank.	Free acid.
1	1.0 c.c.	1.5	13.8 c.c.	12.9 c.c.	0.9 c.c.
2	1.0	2.9	18.2	10.3	7.9
3	1.0	3.8	25.3	11.5	13.8
4	1.0	4.3	25.2	9.9	15.3
5	1.0	4.8	30.0	10.4	19.6
6	1.0	5.2	12.0	9.5	2.5
7	1.0	5.5	5.0	2.8	2.2
8	1.0	5.7	4.6	3.0	1.6
9	1.0	6.0	3.9	2.8	1.1

TABLE III

*Optimum  $p_H$  for lipase using sodium acetate-acetic acid buffer.*

Set No.	Oil.	$p_H$ .	$N/10$ -s o i u m h y d r o x i d e f o r		
			Sample.	Blank.	Free acid.
1	1.0 c.c.	3.8	16.2 c.c.	9.1 c.c.	7.1 c.c.
2	1.0	4.1	19.4	8.2	11.2
3	1.0	4.8	23.1	7.8	15.3
4	1.0	4.9	37.8	6.1	31.7
5	1.0	5.5	15.7	5.2	10.5
6	1.0	5.7	11.6	4.3	7.3
7	1.0	5.9	9.6	3.8	5.8
8	1.0	6.0	6.9	2.6	4.3

From the above tables, it is found that in disodium phosphate-citric acid buffer, the optimum  $p_H$  is 4.8. In sodium acetate-hydrochloric acid buffer, the optimum  $p_H$  is 4.8. In sodium acetate-acetic acid buffer, the optimum  $p_H$  is 4.9. It is inferred that the optimum  $p_H$  for the hydrolysis of the olive oil by ricinus lipase from castor seed is almost constant, i. e., 4.8 to 4.9  $p_H$  varying slightly according to the buffer used. But at the same time, the percentage hydrolysis of olive oil is greatest in sodium acetate-acetic acid buffer and least in phosphate buffer.

*Effect of Buffer Concentration on the Hydrolysis of Olive Oil by Lipase.*—Each set of the experiments consisted of 1 c. c. of olive oil, 2 c.c. of water, 0.1g. of lipase and varying quantities of acetate buffer of 4.9  $p_H$  and incubated for 24 hours at 37°. Always the blank accompanied each sample. After the period of incubation, the contents of each flask were titrated against N/10 sodium hydroxide after adding 25 c.c. of neutral alcohol. The results are given in Table IV.

TABLE IV

Set No.	Oil.	Buffer added.	N/10-sodium hydroxide for		
			Sample.	Blank.	Free acid.
1	1.0 c.c.	1.0 c.c.	30.3 c.c.	1.2 c.c.	29.1 c.c.
2	1.0	2.0	25.0	1.8	28.2
3	1.0	3.0	20.5	2.1	18.4
4	1.0	4.0	18.3	2.3	16.0
5	1.0	5.0	17.4	2.5	14.9
6	1.0	6.0	15.7	3.4	12.3
7	1.0	7.0	14.8	3.8	11.0

From the above table, it is found that the maximum percentage hydrolysis is obtained at the buffer concentration of 1 c. c. and falls gradually as the concentration increases which shows that the percentage hydrolysis goes on decreasing with the increase of buffer concentration.

*Effect of Substrate Concentration on the Hydrolysis of Olive Oil by Lipase.*—Each set of the experiments consisted of varying quantities of olive oil, 2 c. c. of water, 0.1 g. of lipase and 1 c. c. of acetate buffer of 4.9  $p_H$ , incubated for 24 hours at 37°. After the period of incubation, the contents were titrated against N/10 sodium hydroxide after the addition of 25 c. c. of neutral alcohol. Each set was accompanied by a blank. The results are given in Table V. From Table V, it is found that the percentage hydrolysis increases as the concentration of the substrate increases from 1 to 3 c.c. and then gradually decreases as the concentration of the oil increases. Therefore, the maximum percentage hydrolysis is obtained when the concentration of the oil is 3 c. c.

TABLE V

Set No.	Oil	N/10-sodium hydroxide for		
		Sample.	Blank.	Free acid.
1	1.0 c.c.	43.0 c.c.	1.2 c.c.	41.8 c.c.
2	2.0	50.4	1.2	49.2
3	3.0	57.3	1.2	56.1
4	4.0	54.4	1.2	53.2
5	5.0	48.2	1.2	47.0
6	6.0	42.5	1.2	41.3

*Effect of Enzyme Concentration on the Hydrolysis of Olive Oil by Lipase.*—Each set of the experiments consisted of 1 c. c. of olive oil, 2 c. c. of water, 1 c. c. of acetate buffer and varying quantities of the lipase and incubated at 37° for 24 hours. After the period of incubation, the contents were titrated against N/10 sodium hydroxide. Always a blank accompanied each sample. The results are given in Table VI.

TABLE VI

Set No.	Oil	Enzyme added.	N/10-sodium hydroxide for		
			Sample.	Blank	Free acid.
1	1.0 c.c.	0.1 g.	38.1 c.c.	1.6 c.c.	36.5
2	1.0	0.2	38.3	1.6	36.7
3	1.0	0.3	39.1	1.7	37.4
4	1.0	0.4	40.8	2.0	38.8
5	1.0	0.5	46.2	2.0	44.2
6	1.0	0.6	48.9	2.1	46.8
7	1.0	0.7	52.1	2.3	49.8

From the above table, the percentage hydrolysis of olive oil appears to increase with increase in the concentration of the enzyme.

*Effect of Ageing on the Activity of the Lipase.*—There are many factors which affect the activity of the enzymes, e. g., heat, light, time, chemicals, etc., most of which can be prevented except the time factor. So, an investigation was carried out to study the effect of ageing on the activity of the lipase.

The hydrolysis of olive oil by lipase was studied from the time of preparation of the lipase up to a period of 4½ months. Each set of the experiments consisted of 1 c. c. of olive oil, 2 c. c. of water, 0.1 g. of lipase and 1 c. c. of acetate buffer and kept in the incubator at 37° for 20 minutes and then titrated against N/10 sodium hydroxide. Always a blank accompanied each sample. The results are given in Table VII.

TABLE VII

Set No.	Time.	Oil.	Diff. bet. the sample & the blank <sup>a</sup> .	Set No.	Time.	Oil.	Diff. bet. the sample & the blank <sup>a</sup> .
1	0 min.	1.0 c.c.	7.5 c.c.	14	23 days	1.0 c.c.	19.9
2	20	1.0	7.9	15	71	1.0	17.9
3	40	1.0	7.9	16	78	1.0	10.7
4	1 hr.	1.0	8.4	17	86	1.0	10.2
5	24	1.0	13.7	18	93	1.0	9.8
6	2 days	1.0	28.2	19	100	1.0	8.9
7	3	1.0	23.3	20	114	1.0	8.6
8	4	1.0	23.4	21	121	1.0	7.8
9	5	1.0	23.5	22	134	1.0	6.5
10	6	1.0	24.4	23	142	1.0	5.1
11	8	1.0	24.8	24	150	1.0	3.9
12	11	1.0	20.5	25	155	1.0	2.8
13	15	1.0	20.2	26	160	1.0	0.5

\* In terms of c. c. of N/10.NaOH.

From the above table, activity is found to increase up to the 8th day and then it slowly decreases and on the 160th day, it is almost lost. The reason may be due to a small amount of petroleum ether which adheres to the lipase or due to some physical change which may take place in the enzyme after some time.

*Preparation of Different Samples of Lipase.*—As it was found that petroleum ether-dried lipase did not keep its activity constant, several preparations of lipase were made and the effect of ageing on their activities studied to select a sample which would keep its activity fairly constant for a long time.

So, first petroleum ether extract of the lipase was prepared by the usual method and then three samples were prepared by draining for 2 hours—one with petroleum ether, the other with ethyl ether and the third with boiling acetone. All the three samples were completely dried, sieved through a 60 mesh sieve and the fine powder obtained in each case was used for the experiment.

The activities of the three samples were determined at different intervals of time (Table VIII).

From Table VIII, it is found that in the case of petroleum ether-dried and ether-dried samples, the activity first increases and then falls. In case of acetone-dried sample, it is almost constant throughout even though the activity is very low. So, it can be seen that acetone-dried sample retains its activity fairly constant for an appreciably long time.

TABLE VIII

Set No.	Time.	Lipase added.	Diff. bet. the sample and the blank in terms of Petroleum ether sample.	Ether sample.	N/10-NaOH. Acetone sample.
1	0 min.	0.1 g.	7.5 c.c.	5.2 c.c.	1.4 c.c.
2	20	0.1	7.9	5.8	1.4
3	40	0.1	7.9	5.9	1.4
4	1 hour	0.1	8.4	6.1	1.4
5	24 hours	0.1	13.7	10.2	1.4
6	2 days	0.1	23.2	11.5	1.4
7	3	0.1	23.3	12.1	1.4
8	4	0.1	23.4	14.8	1.4
9	5	0.1	23.5	18.2	1.4
10	6	0.1	24.4	16.5	1.4
11	8	0.1	24.8	15.8	1.4
12	11	0.1	20.5	10.2	1.4
13	15	0.1	20.2	9.2	1.4
14	23	0.1	19.9	8.4	1.4
15	71	0.1	17.9	5.3	1.4
16	78	0.1	10.7	4.6	1.4
17	83	0.1	10.2	3.7	1.4
18	93	0.1	9.8	2.9	1.4
19	100	0.1	8.9	2.7	1.4
20	114	0.1	8.6	1.2	1.4
21	120	0.1	7.8	1.1	1.4
22	134	0.1	6.5	0.8	1.4
23	142	0.1	5.1	0.4	1.4
24	150	0.1	3.9	—	1.4
25	155	0.1	2.8	—	1.4
26	160	0.1	0.5	—	1.4

## STUDIES ON 'LIPASE' FROM OIL SEEDS. PART II. SYNTHESIS OF SOME ALIPHATIC ESTERS BY RICINUS LIPASE FROM CASTOR SEEDS

BY G. V. NEVGI AND C. V. RAMAKRISHNAN

Syntheses of some aliphatic esters by ricinus lipase have been carried out in order to study the effect of change of the number of carbon atoms in the alcohol on the enzymic synthesis of esters.

Bodenstein, Dietz and Dietz ( *Z. Elektrochem.*, 1906, 12, 605 ) investigated the formation and the splitting of *iso*amyl butyrate by pancreatic lipase. Rona and Ammon ( *Biochem. Z.*, 1931, 241, 460 ) synthesised *n*-butyl normal butyrate by pig's pancreatic lipase. Since much work has not been done on the synthetic activity of the seed lipase, an attempt was made to study the synthesis of some aliphatic esters using ricinus lipase from castor seeds.

*Synthesis of Butyl Oleate using Different Samples of Lipase.*—Velluz ( *Bull. soc. chim. Biol.*, 1939, 21, 814 ) synthesised butyl oleate using petroleum ether-dried lipase in 17 organic solvents. In the present work, the synthesis of butyl oleate was carried out with different solvents such as petroleum ether, carbon tetrachloride, ether, etc., and the mixture was observed to be homogeneous only in ether solvent. As all the work was carried out with a view to ascertaining the effect of the number of carbon atoms in the alcohol and the acid on the synthesis and hydrolysis of esters, ether was chosen as a solvent for all the experiments.

### EXPERIMENTAL

The chemicals used were (1) butyl alcohol ( $d$  0.809, b.p. 117°), (2) oleic acid ( $d$  0.895, b.p. 286°). In different conical flasks, 5 c.c. of the acid and 3 c.c. of alcohol were added. One gram of lipase and 10 c.c. of the solvent were added to each flask, shaken well and kept in the incubator after corking them well. At different intervals of time, 1 c.c. portion from each flask was taken, 25 c.c. of neutral alcohol added, warmed for some time and titrated against *N*/10 sodium hydroxide. Always the blank accompanied the sample. From the difference in readings between the sample and the blank, the percentage synthesis was calculated. The same experimental procedure was adopted for the rest of the work. The results are given in Table I.

TABLE I  
Solvent : Ether.

Days.	Percentage synthesis of butyl oleate		
	French author.	Present work using petroleum ether sample.	acetone sample.
1	17.8	16.9	6.4
2	31.2	34.8	15.8
3	42.7	43.2	21.6
4	53.4	50.8	32.8
5	58.7	59.5	39.6
6	66.7	70.2	88.5

From the above table, it is found that the results obtained in case of petroleum ether-dried lipase almost agree with those of the French author within the limits of experimental error. The same synthesis, when carried out using acetone-dried lipase, gives the low value. For the rest of the work, acetone-dried lipase was used since it kept its activity fairly constant for an appreciably long time even though the percentage synthesis was low.

*Synthesis of some Aliphatic Esters.*—The synthesis of the following esters belonging to a homologous series was carried out using acetone-dried lipase in ether solvent in order to study the effect of change of the number of carbon atoms in the alcohol on the synthesis of esters by lipase: methyl, ethyl, *n*-propyl, *iso*propyl, *n*- and *iso*butyl, *n*- amyl propionates and butyrates.

Each flask contained equimolecular quantities (0.054 g. mol.) of alcohol and acid, lipase (1g.) and 10 c.c. of the solvent, and incubated at 37°. At different intervals of time, 1 c.c. of it was taken, 25 c.c. of neutral alcohol added, warmed and titrated against *N*/10 sodium hydroxide. Always a blank accompanied the sample. From the difference in readings, the percentage synthesis was calculated. The results are given in Tables II and III.

TABLE II  
Percentage synthesis on the

Esters.	1st day.	2nd day.	3rd day.	4th day.	5th day.	6th day.
Methyl propionate	4.2	4.9	6.2	10.1	11.6	—
Ethyl "	5.1	6.3	10.8	15.4	17.2	—
<i>n</i> -Propyl "	5.5	6.8	9.1	14.8	16.8	18.2
<i>iso</i> Propyl "	12.3	19.1	22.8	25.4	27.6	—
<i>n</i> -Butyl "	12.5	15.6	21.7	26.2	28.4	29.2
<i>iso</i> Butyl "	15.2	25.3	31.8	39.5	43.8	65.4
<i>n</i> -Amyl "	45.1	55.7	71.2	77.2	78.8	—

TABLE III

Esters.	Percentage synthesis on the					
	1st day.	2nd day.	3rd day.	4th day.	5th day.	6th day.
Methyl butyrate	3.28	4.51	6.97	9.0	11.5	—
Ethyl „	3.20	4.21	11.60	16.5	16.5	—
<i>n</i> -Propyl „	8.25	4.60	8.20	9.2	15.8	16.9
<i>iso</i> Propyl „	11.44	18.04	21.76	22.8	26.8	—
<i>n</i> -Butyl „	11.20	13.30	14.80	20.5	24.5	28.3
<i>iso</i> Butyl „	14.70	23.40	33.30	42.9	68.4	—
<i>n</i> -Amyl „	30.80	55.00	61.90	69.3	78.1	—

From Tables II and III, it is found that in case of propionates as well as butyrates, the maximum percentage synthesis increases from methyl to amyl ester. It shows that as the number of carbon atoms in the alcohol increases, the synthesis also increases up to amyl ester.

The synthesis is greater in the *iso* form of the alcohol than in the normal one. The difference in percentage synthesis in the case of *n*-propyl and *isopropyl* esters may be due to the difference in structure (*n*-propyl alcohol is primary, whereas *isopropyl* alcohol is secondary). This proves the fact that the difference in chemical reaction is observed in the case of primary and secondary alcohols. In case of normal and *isobutyl* esters, the difference in percentage synthesis may be due to the difference in density, since the structure is the same for both the esters (*n*-butyl alcohol,  $d$  0.809 ; *isobutyl* alcohol,  $d$  0.812).

*Synthesis of n-Butyl and n-Amyl Esters.*—Butyl and amyl esters of formic, acetic, propionic and butyric acids were synthesised using acetone-dried lipase from castor seeds, and the results are shown in Table IV.

TABLE IV

Esters.	Percentage synthesis on the					
	1st day.	2nd day.	3rd day.	4th day.	5th day.	6th day.
<i>n</i> -Butyl formate	12.8	16.2	22.5	25.6	27.2	—
acetate	11.8	14.5	18.2	22.6	25.4	—
propionate	12.5	15.6	21.7	26.2	28.4	29.2
butyrate	11.2	13.8	14.8	20.5	24.5	28.3
<i>n</i> -Amyl formate	32.4	40.8	63.6	75.8	78.2	—
acetate	26.1	32.1	38.7	74.5	82.9	—
propionate	45.1	55.7	71.2	77.2	76.8	—
butyrate	30.8	55.0	64.9	69.3	78.1	—

From the above table, it is found that the percentage synthesis is almost the same in case of all the four esters, the difference being very small, even though the different acids are used. So, it can be concluded that the synthesis of esters is independent of the number of carbon atoms in the acids and only depends upon the number of carbon atoms in the alcohol. In Table IV, the percentage synthesis of the last four esters is always greater than that of the first 4 esters, which proves that the percentage synthesis depends upon the number of carbon atoms in the alcohol.

# STUDIES ON 'LIPASE' FROM OIL SEEDS. PART III. EFFECT OF HYDROXYL GROUPS IN THE ALCOHOL ON THE SYNTHESIS OF ESTERS BY LIPASE

BY C. V. RAMAKRISHNAN AND G. V. NEVGI

Synthesis of some aliphatic and aromatic esters has been carried out using acetone-dried lipase in order to study the effect of change of the number of hydroxyl groups in the alcohol on the enzymic synthesis of esters.

The synthesis of the following esters was carried out in order to study the effect of change of the number of hydroxyl groups in the alcohol on the synthesis of esters by lipase : ethyl, glycol and glycerine esters of propionic and butyric acids, phenol, resorcinol and pyrogallol esters of benzoic acid. The results are given in the following table.

TABLE I

Esters.	Percentage synthesis on the					
	1st day.	2nd day.	3rd day.	4th day.	5th day.	6th day.
Ethyl propionate	3.0	8.9	9.8	14.9	17.1	18.8
Glycol "	6.3	9.2	19.1	20.8	23.6	22.8
Glycerine "	15.9	20.1	23.9	36.8	39.2	38.5
Ethyl butyrate	3.20	4.21	11.60	16.80	16.50	...
Glycol "	7.50	9.70	18.60	21.70	24.80	23.90
Glycerine "	15.60	18.50	24.80	38.40	37.90	...
Phenol benzoate	2.3	4.8	5.2	11.8	15.6	14.9
Resorcinol "	1.8	3.7	7.4	9.2	12.8	18.6
Pyrogallol "	5.4	8.2	19.5	32.8	31.6	...

From the table it is found that in the aliphatic as well as aromatic series, the percentage synthesis of the ester increases as the number of (OH) group increases in the alcohol. Hence, a clear distinction can be made among mono-, di- and trihydroxy alcohols, since the percentage synthesis of ester increases with the increase in the number of (OH) group in the alcohol.

DEPARTMENT OF BIOCHEMISTRY,  
WADIA COLLEGE, POONA.

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## STUDIES ON 'LIPASE' FROM OIL SEEDS. PART IV. SYNTHESIS OF SOME ESTERS BY LIPASE

BY C. V. RAMAKRISHNAN AND G. V. NEVGI

Synthesis of some more aliphatic and aromatic esters by lipase from castor seeds has been studied in order to find out the effect of alkyl, aromatic, saturated and unsaturated groups on the synthesis of esters.

Some more esters have been synthesised using acetone-dried lipase from castor seeds in order to find out the effect of alkyl, aromatic, saturated, unsaturated groups, etc., on the enzymic synthesis of esters. So the syntheses of butyl stearate, butyl oleate, benzyl benzoate, benzyl butyrate, butyl butyrate, phenol, resorcinol and pyrogallol esters of benzoic acid, ethyl, glycol and glycerine esters of benzoic acid have been carried out and the results are recorded below.

TABLE I

Esters.	Percentage synthesis on the					
	1st day.	2nd day.	3rd day.	4th day.	5th day.	6th day.
A. Butyl stearate	3.7	11.2	18.5	20.2	27.8	35.2
Butyl oleate	10.5	29.7	40.2	50.7	52.5	62.7
B. Phenol benzoate	2.3	4.8	5.2	11.8	15.0	14.9
Ethyl "	1.9	4.2	4.8	8.5	12.0	12.9
Resorcinol "	1.8	8.7	7.4	9.2	12.8	18.0
Glycol "	1.0	2.8	5.0	9.0	11.2	16.8
Pyrogallol "	5.4	10.2	10.5	32.8	31.6	...
Glycerine "	4.8	7.5	18.2	28.6	30.2	29.8
C. Benzyl benzoate	8.9	14.2	22.8	25.6	28.9	27.2
Butyl butyrate	11.2	13.8	14.8	20.5	24.5	28.3
Benzyl "	7.5	12.9	21.8	23.2	24.0	23.9
Butyl benzoate	7.0	9.6	11.2	14.8	16.9	15.8

From Table I (A) it is found that the percentage synthesis of the ester is always more in case of an unsaturated acid than a saturated one. So a clear distinction can be made between saturated and unsaturated compounds, (*i.e.*, single and double bond compound), since the percentage synthesis of the ester increases with unsaturation, which proves evidently the statement that unsaturated compounds are more reactive.

From Table I (B) it can be inferred that even though the percentage synthesis of the ester increases as the number of (OH) group increases in the alcohol in the aliphatic as well as aromatic series, still the percentage is always more in case of an aromatic compound than the aliphatic one.

From Table I (C) it is found that the percentage synthesis of the ester is always more when both the alcohol and acid used are aromatic than when both are aliphatic. Further, the percentage synthesis in case of esters where both alcohol and acid belong to the same family (*i.e.*, aliphatic or aromatic) is always more than one in which they belong to different families.

## STUDIES ON 'LIPASE' FROM OIL SEEDS. PART V. SYNTHESIS OF SOME ESTERS BY LIPASE

By C. V. RAMAKRISHNAN AND G. V. NEVGI

Synthesis of some aliphatic esters by ricinus lipase has been carried out by taking different molecular quantities of acid and alcohol in order to study the effect of change of molecular quantities of the reacting substances on the synthesis of esters.

An attempt has been made to study the effect of change of molecular quantities of alcohol and acid on the synthesis of esters by ricinus lipase by taking at first different molecular quantities of alcohol, keeping the quantity of acid constant, and then different quantities of acid keeping the quantity of alcohol constant.

First of all, the syntheses of aliphatic butyrates as well as amyl formate, acetate, propionate and butyrate were carried out by taking constant amount of acid (0.054 g. mol.) and varying the amount of the alcohol.

### EXPERIMENTAL

In the first series, each set of the experiments consisted of 0.054 g. mol. of acid and different molecular quantities of different alcohols (*i.e.*, 0.028 g. mol., 0.054 g. mol., and 0.108 g. mol.), 1 g. of lipase, 10 c.c. of ether solvent and a few drops of toluene, and kept in the incubator at 37°. At different intervals of time, 1 c.c. of it was taken, 25 c.c. of neutral alcohol added, warmed and titrated against *N*/10 sodium hydroxide. Always, a blank accompanied the sample. From the difference in readings between the sample and the blank, the percentage synthesis was calculated. The results are given in Table I.

TABLE I

Esters.	Acid=0.054 g. mol.		Alcohol=0.028 g. mol.				
			Percentage synthesis on days.				
	1st.	2nd.	3rd.	4th.	5th.	6th.	7th.
Methyl butyrate	1.1	2.4	3.9	5.0	6.2	7.1	6.8
Ethyl "	0.9	2.0	4.9	7.2	6.8	...	...
<i>n</i> -Propyl "	1.6	3.0	4.2	5.2	7.6	8.2	8.0
<i>iso</i> Propyl "	4.8	8.9	11.2	12.3	14.5	13.8	...
<i>n</i> -Butyl "	5.1	7.2	8.1	10.9	13.2	15.6	14.8
<i>iso</i> Butyl "	6.3	9.5	14.4	15.6	20.2	25.8	24.4
<i>n</i> -Amyl "	12.7	18.8	22.1	28.9	33.3	39.5	37.8
<i>n</i> -Amyl formate	15.2	16.6	21.9	25.6	31.8	36.7	35.8
" acetate	13.1	15.7	17.8	20.8	24.9	27.8	32.3
" propionate	20.2	27.5	35.2	38.5	37.8	...	...
" butyrate	12.7	18.8	22.1	28.9	33.2	39.5	37.8

TABLE I (contd.)

Esters.	1st.	2nd.	3rd.	4th.	5th.	6th.	7th.
	Acid=0.054 g. mol.			Alcohol=0.054 g. mol.			
Methyl butyrate	3.28	4.5	6.9	9.0	11.5	...	...
Ethyl "	8.2	4.2	11.6	16.8	16.5	...	...
<i>n</i> -Propyl "	3.8	4.6	8.2	9.2	15.8	16.9	...
<i>iso</i> Propyl "	11.4	18.0	21.8	22.8	26.8	...	...
<i>n</i> -Butyl "	11.2	13.3	14.8	20.5	24.5	23.8	...
<i>iso</i> Butyl "	14.7	23.4	33.3	42.9	63.4	...	...
<i>n</i> -Amyl "	30.8	55.0	64.9	69.3	78.1	...	...
<i>n</i> -Amyl formate	32.4	40.8	68.6	75.8	78.2	...	...
" acetate	26.1	32.1	38.7	74.5	82.9	...	...
" propionate	45.1	55.7	71.2	77.2	76.8	...	...
" butyrate	30.8	55.0	64.9	69.3	78.1	...	...
	Acid=0.054 g. mol.			Alcohol=0.108 g. mol.			
Methyl butyrate	5.2	7.8	10.2	14.2	12.8	...	...
Ethyl "	4.7	6.8	12.3	17.2	18.5	...	...
<i>n</i> -Propyl "	5.7	7.8	13.9	19.5	23.8	22.8	...
<i>iso</i> Propyl "	10.9	21.8	27.3	29.8	31.6	...	...
<i>n</i> -Butyl "	11.2	15.6	17.8	28.2	35.6	34.8	...
<i>iso</i> Butyl "	15.2	18.9	21.8	29.3	37.8	43.5	...
<i>n</i> -Amyl "	22.8	32.7	48.3	55.6	68.2	79.5	...
<i>n</i> -Amyl formate	23.6	39.8	52.7	68.7	72.8	71.9	...
" acetate	32.3	37.8	51.7	59.8	65.8	77.9	...
" propionate	22.1	28.5	37.8	52.3	69.1	75.6	...
" butyrate	22.8	32.7	48.3	55.6	68.2	79.5	...

In the second series, the synthesis of *n*-amyl butyrate was studied in detail first by keeping the quantity of butyric acid constant and taking different molecular quantities of amyl alcohol and then by keeping the quantity of alcohol constant and taking different molecular quantities of the acid. The results are given in Table II.

TABLE II

*Synthesis of n-amyl butyrate.*

Alcohol.	Percentage synthesis on the						
	1st day.	2nd day.	3rd day.	4th day.	5th day.	6th day.	7th day.
	Acid=0.054 g. mol.						
0.0108 g. mol.	5.2	6.8	9.5	15.2	16.5	17.8	16.9
0.0270	12.3	17.8	21.8	27.8	31.2	38.5	36.2
0.0540	30.8	55.0	64.9	69.3	78.1	...	...
0.0810	40.2	52.8	59.3	64.8	70.2	76.0	75.8
0.1080	22.8	32.7	48.3	55.6	68.2	79.5	...
0.2160	30.8	40.1	49.8	56.2	72.8	82.5	81.5
0.6480	35.8	45.6	51.2	59.6	68.0	89.8	88.8
1.296	42.3	51.8	62.1	72.8	89.5	91.4	90.8
2.592	50.2	58.9	65.6	79.8	82.1	92.8	90.5

TABLE II (*contd.*)

Acid.	Percentage synthesis on the						
	1st day.	2nd day.	3rd day.	4th day.	5th day.	6th day.	7th day.
	Alcohol=0.054 g. mol.						
0.0108 g. mol.	12.3	19.5	28.8	30.2	36.5	35.1	
0.0270	20.2	36.6	41.2	48.9	58.2	57.5	
0.0540	30.8	55.0	64.9	69.8	78.1		
0.0810	32.9	57.8	62.1	68.5	72.8	78.1	75.0
0.1080	35.9	48.2	59.6	65.1	70.9	78.1	79.2
0.2160	40.2	49.0	62.8	68.1	76.2	80.1	79.2
0.6480	28.2	39.8	45.6	50.1	65.7	78.2	81.8
1.296	15.2	36.5	51.9	70.2	81.2	88.5	87.2
2.592	43.8	59.8	65.7	70.9	79.2	89.7	89.7

From Table I it is found that the percentage synthesis of the ester increases in the order : 0.028 g. mol., 0.054 g. mol. and 0.108 g. mol. quantities of alcohol taken for the experiment. In each case (*i.e.*, when molecular quantity is constant) the percentage synthesis increases from methyl to amyl butyrate and the synthesis is always more in the *iso* form than in the *normal* one ; further the percentage synthesis is the same when different acids are used.

From Table II it is found that the percentage synthesis goes on increasing as the molecular quantity of either the acid or the alcohol increases till it reaches a maximum value. The maximum percentage synthesis is reached when the concentration of the alcohol or the acid is 2.592 g. mol.

From the above results, it can be concluded that the percentage synthesis increases with the increase in molecular quantities of alcohol or acid taken for the experiment up to a certain limit.

## NATURE OF CLAY MINERALS PRESENT IN SAKRAND SOIL

BY B. CHATTERJEE

The chemical composition and electrochemical and viscous properties attribute a predominantly illitic nature to the Sakrand clay.

The properties of the subfractions of the entire clay fraction isolated from a saline soil from Sakrand (Sind) have been dealt with in a previous publication (Chatterjee and Gupta, *Science & Culture*, 1946-47, 12, 57). The present note records the results of chemical, electrochemical, viscous and mineralogical studies of the Sakrand clay. This work was undertaken to obtain information on the nature of clay minerals (*i. e.*, secondary aluminosilicate minerals) present in a saline soil and also to supplement the data already obtained, since it has been proved beyond doubt that there is not a single soil property which is not directly or indirectly connected with the nature and amounts of clay minerals present in it (Joffe, "Pedology", 1949). The clay fraction, separated according to the International method, was converted into hydrogen clay (H-clay) by repeated leaching with 0.03N hydrochloric acid, followed by washing with water and was finally dispersed in distilled water.

**Chemical Composition.**—The percentages of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{K}_2\text{O}$  of the H-clay determined by fusion analysis are 55.10, 23.31, 11.28, 3.50 and 6.60 respectively. The H-clay did not seem to contain any measurable amount of calcium. The presence of the high amount of potassium suggests that the mineral constituent of the Sakrand clay belongs to the illite (hydrous mica) group. The general formula



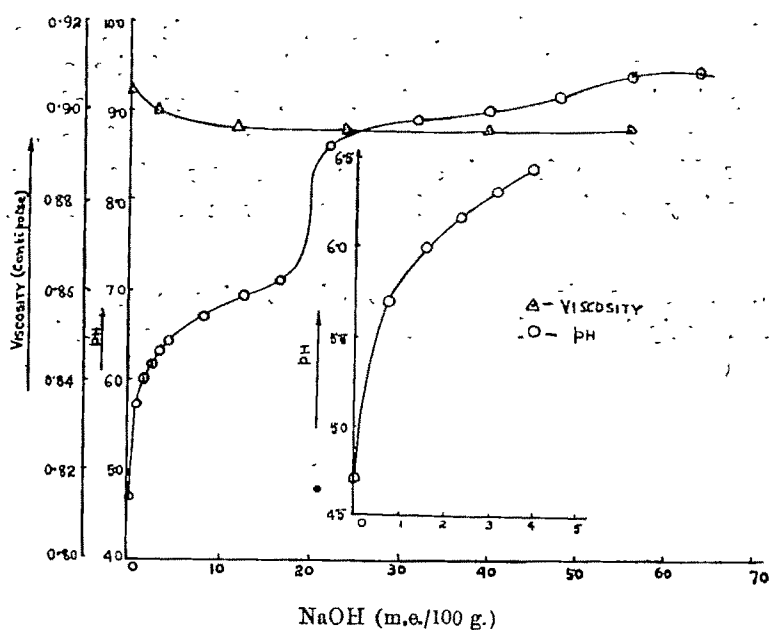
with  $y$  varying from 1.0 to 1.5, has been suggested (Grim *et al.*, *Amer. Min.*, 1937, 22, 813) for minerals of this group. The amount of illite in the Sakrand clay comes to over 90% when the analytical data are fitted in the above formula. The presence of unweathered potassium bearing primary minerals, *e.g.*, feldspar, in the Sakrand clay is, however, not altogether improbable. In that case, the percentage of illite will diminish correspondingly.

**Electrochemical Properties.**—The potentiometric titration curve (Fig. 1) with NaOH of the H-clay, prepared from the Sakrand soil, shows a sharp inflexion at  $\text{pH}$  7.9 and a very weak one at  $\text{pH}$  9.3 and in this respect it is somewhat similar to those of H-kaolinite. The resemblance is, however, superficial. As for instance, the base exchange capacities (b.e.c.) calculated at the two inflexion points (*viz.* 20.0 and 52.0 milliequivalents per 100 g.) are considerably higher than the corresponding values for kaolinites (Mukherjee

and Mitra, *Nature*, 1944, 154, 821 ). Further, the ratio of the b. e. c' s at the first and second inflexion points in the titration curve of the Sakrand clay is 2.6, while the corresponding value for H-kaolinite is 2.0.

*Viscous Property.*—Apart from a slight initial decrease, the viscosity of 0.55% suspensions of the H-clay, prepared from the Sakrand soil, does not appear to change on the addition of increasing amounts of NaOH ( Fig. 1 ). This observation indicates the absence of a marked amount of montmorillonite in this clay ( Mukherjee and Mitra, *loc. cit.* ). The viscosity-alkali concentration curve appears to be characteristic of illite ( Indra and Neogyi, unpublished ) or of kaolinite ( Mukherjee and Mitra, *J. Coll. Sci.*, 1946, 1, 141 ) The nature of the potentiometric curve and high value of the b. e. c., however, suggest the absence of marked amounts of kaolinite in this clay

FIG. 1



*Mineralogical Studies.*—The percentages of heavy and light minerals present in the fine and coarse sand fractions have been determined to gain information, if possible, on the genesis and development of the Sakrand soil. The light and heavy fractions were separated by means of bromoform using a hand centrifuge. These fractions were then examined under a petrographic microscope. The results have been summarised in Table I.

TABLE I

	Light fraction.	Heavy fraction.
Coarse sand	93.5% by weight (plagioclase* and shells)	6.5% by weight (biotite*, shells and magnetite)
Fine sand	98.0% by weight [plagioclase*, quartz (few) and microcline]	7.0% by weight (biotite, 50% hornblende, 25% rest**, 25%)

\* Dominant mineral.

\*\* Rest denotes tourmaline, garnet, muscovite, zoisite, calcite and epidote.

The occurrence of the micaceous minerals in the sand fractions is in conformity with the predominantly illitic nature of the Sakrand clay. The presence of plagioclase, biotite and hornblende in large amounts indicates that weathering has not proceeded to any great extent in this soil. The very low percentage of quartz and of the alteration products of biotite and hornblende also point to the immature nature of the soil. The results of petrographic analysis suggest that the Sakrand clay is probably derived from the Tertiary Fossiliferous Limestone formation of the hill ranges lying to the west and consisting mainly of limestone and dolomite with subordinate amount of shale.

The author takes this opportunity to offer his sincere thanks to Dr. S. R. Sen Gupta, Principal, Bengal Engineering College, for his kind interest in the work.

## PARACHOR OF MERCURIC CHLORIDE

By R. P. SHUKLA AND W. V. BHAGWAT

Parachor of mercuric chloride in water, in ethyl acetate and pyridine and also methyl alcohol has been determined. The low results in water indicate that mercuric chloride is appreciably ionised and hence is truly an electrovalent compound.

Bhagwat and Toshniwal (this *Journal*, 1942, 19, 493) have given results for the parachor of mercuric chloride in water and some organic solvents. The results are not consistent. It seems that the deviation is due to the fact that mercuric chloride is not very soluble in these solvents, and hence the molar fraction is very low. A slight error therefore is highly magnified. To get more accurate results we have used cathetometer reading up to 0.02 of a mm. for noting the height of the liquid in Jagar's maximum pressure method. Our results are more consistent and therefore more reliable and they are recorded below.  $x$  represents molar fraction of mercuric chloride.

TABLE I

### *Mercuric chloride in water.*

Parachor of water as determined = 52.34.

Temp.	$d.$	$r.$	$P_m.$	$P_x.$
		$x=0.003454$		
70.0°	1.020	64.04	52.42	81.25
65.0°	1.024	65.22	52.43	81.23
		$x=0.007142$		
62.99°	1.064	62.99	52.53	88.62
63.0°	1.068	64.04	52.53	82.62
65.24°	1.073	65.24	52.54	84.05
		$x=0.009545$		
74.0°	1.093	62.92	52.60	82.75
66.0°	1.096	63.54	52.63	85.90
58.0°	1.098	64.02	52.60	82.75

TABLE II

### *Mercuric chloride in methyl alcohol.*

Parachor of methyl alcohol as determined = 88.81.

		$x=0.08556$		
Temp.	$d.$	$r.$	$P_m.$	$P_x.$
22.2°	0.9991	26.60	92.06	180.4
25.0°	0.9942	26.16	92.23	185.0
30.0°	0.9900	25.67	92.12	182.0
		$x=0.04498$		
20.2°	1.005	22.74	92.99	180.0
25.0°	0.9970	22.14	93.13	185.0
30.0°	0.9858	21.09	92.97	181.6



TABLE III

*Mercuric chloride in ethyl acetate.*

Parachor of ethyl acetate as determined = 213.2.

Temp.	d.	r.	$P_m$ .	$P_x$ .
$\alpha = 0.07775$				
22.8°	1.088	25.23	210.6	180.0
25.0°	1.085	25.02	210.8	182.5
30.0°	1.079	24.63	211.0	185.4
$\alpha = 0.07213$				
22.8°	1.077	25.17	210.9	181.0
25.0°	1.074	24.84	211.0	183.0
30.0°	1.068	24.48	211.1	185.4

TABLE IV

*Mercuric chloride in pyridine.*

Parachor of pyridine as determined = 198.5.

Temp.	d.	r.	$P_m$ .	$P_x$ .
$\alpha = 0.07206$				
22.1°	1.197	42.31	197.9	190.1
25.0°	1.192	41.58	197.6	193.2
30.0°	1.181	41.58	198.1	192.5
$\alpha = 0.7185$				
22.1°	1.199	43.01	198.2	192.5
25.0°	1.195	42.58	198.0	180.8
30.0°	1.195	41.58	197.3	180.0

The theoretical value for mercuric chloride is about 180. It will be seen that the value obtained in water is much lower, while in organic solvent the value corresponds to the theoretical, except in case of pyridine, where the value is somewhat higher.

Mercuric chloride is abnormal in its behaviour. Although it is an inorganic salt, it is more soluble in organic solvents than in water. Its conductivity at low temperature is low, but increases rapidly with temperature and shows an abnormally high temperature coefficient. Its coagulating power inspite of its low conductivity is very high, which indicates a high degree of ionisation in contradiction to conductivity results.

Since mercuric chloride is not expected to ionise in organic solvents, the results should approach the theoretical value 180. This has been found to be so. The high results with pyridine are obviously due to its peculiar behaviour in forming complexes of the type  $\text{HgCl}_2 \cdot 2\text{Py}$ ,  $\text{HgCl}_2 \cdot 4\text{Py}$ , etc.

In a series of papers published from these laboratories (this *Journal*, 1944, 21, 53, 62; 1949, 26, 39) it is established that inorganic salts due to their ionisation show very low results. Conversely therefore, low results should be taken to indicate ionisation. Bhagwat and Tosniwal's results have failed to indicate any ionisation. We therefore have determined our value of parachor of mercuric chloride at higher temperatures and our results give low values of parachor than the calculated one and thus establish ionisation.

## DIPOLE MOMENT AND STRUCTURE OF HEXACHLOROCYCLOHEXANES

BY S. K. K. JATKAR AND (MISS) S. B. KULKARNI

Commercial hexachlorocyclohexane was separated into four isomers:  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  melting at  $158^\circ$ ,  $309^\circ$ ,  $112.5^\circ$  and  $188^\circ$  respectively, by fractional crystallisation from methyl alcohol. The dielectric constants and densities of the isomers were measured in different solvents and the dipole moments of the isomers were calculated by applying the new equation. The results are used to ascribe the structures to the isomers.  $\beta$  and  $\delta$  isomers have symmetrical structures. The moment  $2.55D$  of  $\gamma$ -isomer, which has five equatorial and one polar chlorine atoms, is explained as the vector of two C—Cl bonds at tetrahedral angle, the remaining bonds cancelling out. The moment  $1.7D$  for the  $\alpha$ -isomer is explained on the basis of the flexible boat form which has the highest energy content and which forms 70% of the product. The heat of vaporisation of the  $\beta$ -isomer is lowest (11.87 K cal.) and of others, about 13.6 K cal. The infra-red spectra support the structures assigned to the various isomers. The study of alkaline dehydrochlorination of the isomers indicates the order of hydrolysis as  $\alpha > \delta > \gamma > \epsilon$ , the  $\beta$ -isomer being inert. The correlation between the insecticidal property and the dipole moment of the isomers reveals the fact that in this series the dipole moment varies linearly with the logarithm of the mortality coefficient  $K$  and that the  $\gamma$ -isomer, which possesses outstanding insecticidal properties, has high dipole moment.

The determination of the molecular structure of different isomers of hexachlorocyclohexanes would be of great interest, as one of the isomers is well known to be a powerful insecticide.

Hexachlorocyclohexane was first prepared by Faraday (1825) by passing a current of chlorine in benzene in the presence of sunlight. Matthews (*J. Chem. Soc.*, 1891, 59, 166) showed that it contained two isomers. Van der Linden (*Ber.*, 1912, 45, 231) proved the existence of four isomers. Thomas (cf. Slade, *Chem. Ind.*, 1945, 64, 314) showed that the  $\gamma$ -isomer was the most powerful insecticide. Recently Kauer *et al.* (*Ind. Eng. Chem.*, 1947, 39, 1335) have isolated the fifth isomer  $\epsilon$  (m. p.  $219^\circ$ ) and shown that it is non-toxic to insects.

Williams and Fogelberg (*J. Amer. Chem. Soc.*, 1931, 53, 2098-) have reported the dipole moments for the  $\alpha$ - and  $\beta$ -isomers. Hassel (*Z. physikal. Chem.*, 1932, B15, 373) showed that the moment of  $\beta$ -isomer was zero. Slade (*loc. cit.*) has stated that of the 16 possible isomers of hexachlorocyclohexanes only four are strainless (chair) forms. According to Daasch (*Ind. Eng. Chem., Anal. Ed.*, 1947, 19, 779), in addition to the four chair forms of hexachlorocyclohexanes, there is one boat (flexible) form which could also occur as a mirror-image. Since the  $\epsilon$ -isomer concentration is the lowest (3%) in the mixture, the boat form corresponds to the configuration of  $\epsilon$ -isomer according to Daasch (*loc. cit.*).

The present authors (*Proc. Indian Sci. Cong.*, 1949, Part III, p. 26; *Science & Culture*, 1949, 11, 482; *Chem. Abstract*, 1949, 43, 6877) have isolated the

four isomers,  $\alpha$ ,  $\beta$ ,  $\delta$  and  $\gamma$ , from the commercial mixture of hexachlorocyclohexane and determined the dipole moments with a view to substantiating the structures assigned to them and also to correlating the insecticidal property with the data on dipole moment.

## EXPERIMENTAL

### *Preparation of Pure Isomers from the Crude Materials*

The four isomers,  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ , were isolated from the crude material by the method worked out by Smart (cf. Slade, *loc. cit.*). The crude hexachlorocyclohexane was treated with a small amount of methyl alcohol in which the  $\alpha$ - and  $\beta$ -forms are relatively insoluble. Separation of the solid (I) leaves a solution containing the  $\gamma$  and  $\delta$  and other lower chlorinated substances and very little  $\alpha$  and  $\beta$ . The solution was evaporated to half its volume, when a small crop of practically pure  $\gamma$  (II, m.p. 110°) was obtained. Next crop obtained on further evaporation, contained  $\gamma$ , little  $\alpha$  and  $\beta$  (III). Pure  $\gamma$  was prepared from (II) by recrystallising twice from chloroform and four times from carbon tetrachloride. Pure  $\delta$  was obtained with difficulty from (III) by pouring the methanol solution in petroleum ether and finally recrystallising from chloroform.  $\alpha$  and  $\beta$  were isolated from (I) by treatment with chloroform in which  $\beta$  was practically insoluble (0.3%) and pure  $\alpha$  was obtained by recrystallising from benzene. The residue, containing mostly  $\beta$ , was washed with chloroform to remove traces of impurities of other isomers and was finally recrystallised from acetone. The melting points of pure isomers are :  $\alpha$ , 158°;  $\beta$ , 309°;  $\gamma$ , 112.5°;  $\delta$ , 138° in agreement with the values reported by others.

The dielectric constant and density of these isomers were measured in benzene, carbon tetrachloride and dioxane; the dielectric constant of pure molten  $\gamma$ -isomer was also measured between 113° and 150°. Dipole moment was calculated by applying the new equation (Jatkar *et al.*, *J. Ind. Inst. Sci.*, 1946, 28A, Part II),

$$P = (\epsilon - 1) M/d; P_R = (n^2 - 1) M/d;$$

$$P - P_R = \frac{4\pi N\mu^2}{kT} \text{ for pure liquid and}$$

$$p_{12} = \frac{\epsilon_{12} - 1}{d_{12}} = p_1 w_1 + p_2 w_2 \text{ and } P_2 = p_2 M_2 \text{ for solutions,}$$

where  $w_2$  is the weight fraction of the solute. The value of the electronic polarisation ( $P_R$ ) calculated from the refractive index and density given by Hassel (*Tids. kjmi Berg.*, 1930, 81, 126) is 270. The results are given in the following tables.

TABLE I

*Dielectric constant and dipole moment of hexachlorocyclohexane.*

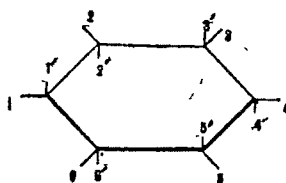
$t^\circ$ .	Solvent.	$w_2$ .	$\epsilon$ .	$d$ .	$P_2$ .	$\mu \times 10^{18}$ .
<i><math>\alpha</math>-Hexachlorocyclohexane.</i>						
25°	$C_6H_6$	(a) { 0.0000	2.376	0.8735	(114.1)	...
		0.0012	2.285	0.8755	835.8	1.74
		0.0031	2.298	0.8788	838.7	1.75
		0.0061	2.319	0.8830	851.6	1.77
		0.0091	2.340	0.8877	852.2	1.77
25°		0.0682	2.3841	0.9016	743.0	1.70
	"	0.0729	2.4035	0.9070	770.9	1.71
40°		0.0682	2.3663	0.8853	740.0	1.67
	"	0.0729	2.3679	0.8828	752.1	1.70
25°	$C_4H_8O_2$	0.1608	2.5365	1.0973	747.2	1.70
40°	"	0.1608	2.4798	1.0826	690.0	(1.80)
<i><math>\beta</math>-Hexachlorocyclohexane.</i>						
28°	$C_4H_8O_2$	0.0220	2.2456	1.0360	191.0	0.00
		0.0396	2.1854	1.0776	...	0.00
<i><math>\gamma</math>-Hexachlorocyclohexane (Gammexane).</i>						
25°	$C_6H_6$	0.0780	2.5886	0.9092	1471.9	2.53
		0.1218	2.7546	0.9267	1457.7	2.53
40°	"	0.0780	2.5485	0.8925	1447.0	2.57
	"	0.1218	2.7023	0.9139	1385.0	2.58
25°	$CCl_4$	0.0286	2.4037	1.5910	1840.0	2.50
		0.0319	2.4310	1.5905	1833.0	2.52
40°	"	0.0286	2.3695	1.5634	1280.0	2.50
	"	0.0319	2.4037	1.5631	1360.0	2.53
25°	$C_4H_8O_2$	0.0564	2.4929	1.0528	1587.0	(2.60)
		0.0799	2.5446	1.0627	1351.0	2.53
40°	"	0.0564	2.4476	1.0364	1478.0	(2.61)
	"	0.0799	2.5058	1.0464	1300.0	2.53
<i><math>\delta</math>-Hexachlorocyclohexane.</i>						
25°	$C_6H_6$	0.0537	2.2406	0.8881	90.5	0.0
40°	"	0.0537	2.2375	0.8806	124.5	0.0
$t^\circ$ .	$\epsilon$ .		$d$ .	$P$ .	$\mu \times 10^{18}$ .	
<i><math>\gamma</math>-Hexachlorocyclohexane (Gammexane), (pure molten liquid).</i>						
159°	6.900		1.556	1102.8	2.55	
142°	7.293		1.574	1162.8	2.58	
129°	7.559		1.588	1201.3	2.59	
113°	7.857		1.604	1243.8	2.60	
22°	Solid }					
	2.558 }					

(a)  $f_2$ , mole fractions (data from Williams and Fogelberg, *J. Amer. Chem. Soc.*, 1931, 53, 2098, 1938). The rest by the present authors.

## DISCUSSION

Sachse (*Ber.*, 1896, 13, 1363) in his theory of strainless ring postulated that a ring such as *cyclohexane*, would be able to take two configurations, now commonly designated as C or boat form and Z or chair (planar) form. Hassel (*loc. cit.*) investigated the properties of monochloro*cyclohexane* and came to the conclusion that in the Z (chair) form, chlorine was able to assume two positions which were interconvertible in the C form. The two types of valence bonds, parallel and perpendicular to the plane of the ring, may be termed equatorial and polar (cf. Beckett, *J. Amer. Chem. Soc.*, 1947, 69, 2488). Of the two hydrogen atoms on each carbon atom, one is polar and one is equatorial.

In the planar (Z) form, there are three polar hydrogens (1', 3', 5') above the plane of the ring, and three (2', 4', 6') below the plane of the ring, while the six hydrogen atoms (1, 2, 3, 4, 5, 6) lie on the belt around the carbon ring.



Based upon Z (planar, rigid) form of the *cyclohexane* ring, there are 16 possible configurations for hexachloro*cyclohexanes*, but owing to the strain involved in the close approach of the chlorine atoms, only four strainless configurations are possible, out of which one can exist as the mirror-image. As the two types of bonds, polar and equatorial, are interconvertible in the C (flexible) form of the *cyclohexane* ring, there is only one strainless form of hexachloro*cyclohexane* in the C (flexible) form. Therefore, the possible number of isomers of hexachloro*cyclohexanes* is five, four in rigid Z form and one in flexible C form.

*Dipole Moment and Structure of the Isomers*

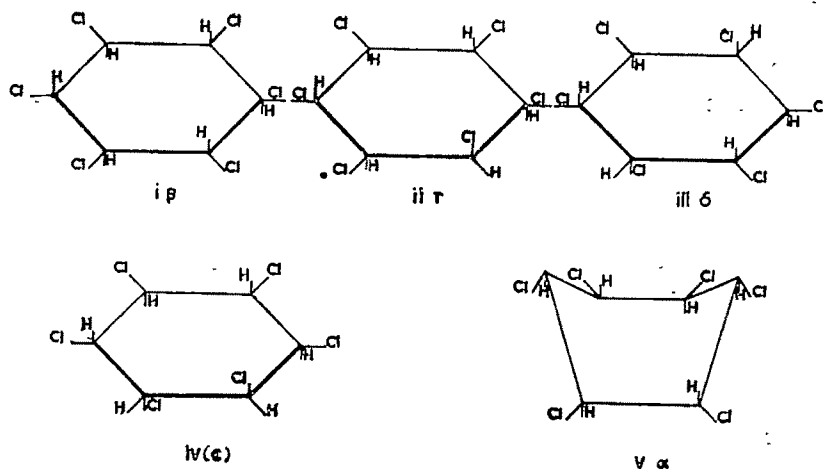
*β-Isomer.*—Dickinson and Bilike (*ibid.*, 1928, 50, 764) on X-ray study of the *β*-isomer (m. p. 309°) found that the *cyclohexane* ring in *β* has centrosymmetrical structure, with all the chlorine atoms evenly distributed. The dipole moment of *β*-isomer has been reported to be 0.7 in benzene and 2.0 in dioxane by Williams and Fogelberg (*loc. cit.*). The recalculated value of the moment from data in benzene is 0.2. However, Hassel (*loc. cit.*) has shown that the moment of *β* in benzene is zero and the present work confirms that the moment of *β*-isomer (m. p. 309°) in dioxane also is zero. The structure of the *β*-isomer is (i) in which there are 6 equatorial chlorine atoms and 6 polar hydrogen atoms above and below the plane of the ring.

*γ-Isomer.*—The observed moment for *γ*-isomer (m. p. 112.5°) is 2.55, which can be explained on the basis of the structure (ii) which has five

equatorial and one polar chlorine atoms. Two pairs of equatorial chlorine atoms oppose each other, out of the remaining, one equatorial chlorine and one polar chlorine make a tetrahedral angle; taking the bond moment C—Cl, 1.69 and C—H, 0.4, the resultant vector moment for  $\gamma$  is 2.5 which is in very good agreement with the observed value.

$\delta$ -Isomer.—The moment of  $\delta$ -isomer (m. p.  $138^\circ$ ) is zero which could be explained by a configuration with two polar chlorine atoms (1', 4') and four equatorial (2, 3, 5 and 6) chlorine atoms, which form three opposite pairs, making the isomer a symmetrical molecule.

$\alpha$ -Isomer.—The observed moment of  $\alpha$ -isomer (m. p.  $158^\circ$ ), 1.7D, is in agreement with the recalculated data of Williams and Fogelberg (*loc. cit.*). According to Slade (*loc. cit.*) the configuration (IV) with two polar (1', 2') and four equatorial (3, 4, 5, 6) chlorine atoms represents the  $\alpha$ -isomer. The moment calculated for this configuration is 3.6D. Hence, this assumption is incorrect. The moment calculated for the flexible structure, (boat or C form) with two chlorine atoms on the stern and the bow of the boat and the remaining four chlorine atoms equatorial, is 1.70D, in agreement with the observed value for the isomer  $\alpha$ , melting at  $158^\circ$ . It is interesting to note that  $\alpha$ -isomer forms 70% of the total product due to its strainless structure, which has accordingly a low toxicity. This finding is of interest in view of the possibility of converting the flexible form into some of the more useful rigid form e. g.,  $\gamma$ -isomer by heating with aluminium trichloride.

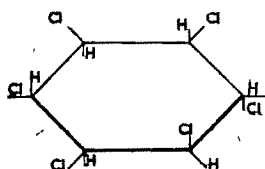


$\epsilon$ -Isomer.—According to Daasch (*loc. cit.*)  $\beta$ - and  $\epsilon$ -isomers are spectrally similar in shorter wave-length regions (2 to 10  $m\mu$ ), the most striking feature of these two spectra being the simplicity when compared with those of the

other isomers. Naturally it follows that the *cyclohexane* ring in the  $\beta$ - and  $\epsilon$ -isomers should have the same forms, either rigid Z (chair) or flexible C (boat) forms and as the X-ray and electron diffraction data (Hassel, *Chem. Zentr.*, 1942, II, 878) have established the existence of Z form of the *cyclohexane* ring in the  $\beta$ -isomer (m. p.  $309^\circ$ ) it is quite evident that the  $\epsilon$ -isomer (m.p.  $219^\circ$ ) should also have Z form and not the flexible form as assumed by Daasch. It will be interesting to investigate the dipole moment of this isomer, which should be  $3.6D$ .

The structures of the isomers are therefore, as shown above.

Subsequent work has been published on the structures of the various isomers of hexachlorocyclohexane. By means of the Fourier-projections of the gammexane cell Bijvoet (*Rec. trav. chim.*, 1948, 67, 777) has assigned 1', 2', 3', 4, 5, 6, *i. e.*,



configuration to  $\gamma$ -isomer. Since due to steric hinderance no two polar Cl atoms can be present in *meta* position, this author has predicted deformation of valency angles between the two C—Cl bonds. The dipole moment of the isomer with this configuration should be very high (about  $3.55D$ ), whereas the observed moment is  $2.5D$ . Bastiansen and Hassel (*Research*, 1949, 2, 248) have ascribed structure (iii) for  $\epsilon$ -isomer and have reported the dipole moment of this isomer to be zero. However, no data are available. Present authors have already shown that the  $\delta$ -isomer with configuration (iii) has zero dipole moment.

#### *Physical and Chemical Properties of the Hexachlorocyclohexanes*

In pure state the isomers are well defined colorless crystals, practically insoluble in water and soluble in almost all organic solvents. Of the isomers,  $\delta$  is the most soluble and  $\beta$  is the least soluble in organic solvents, which is explained by the fact that the solubility is inversely proportional to the number of peripheral chlorine atoms, the  $\beta$ -isomer with maximum number (6) of peripheral chlorine atoms being the least soluble. The melting points of the isomers given in the following table are in agreement with the literature values (Slade, *loc. cit.*). The M. p. of  $\beta$ -isomer ( $196^\circ$ - $210^\circ$ ) reported by Daasch (*loc. cit.*) is very low and is probably in error. The melting point increases with the number of peripheral chlorine atoms, the  $\beta$ -isomer with 6 peripheral chlorine atoms has the highest melting point ( $309^\circ$ ).

TABLE II

Isomer.	Occurrence.	M. p.	Solubility in C <sub>6</sub> H <sub>6</sub> .	Obs. $\mu \times 10^{18}$ .	Mortality coefficient $K \times 10^3$ .
	(b)	(a)	(c)	(a)	(a)
$\alpha$	70%	158°	11.8	1.7	67.2
$\beta$	5	309°	1.12	0.0	0.24
$\gamma$	10-12	112.5°	33.7	2.55	160.80
$\delta$	10	185°	46.2	0.0	19.2
$\epsilon$	8	219°(c)	14.8	—	—

(a) Present authors.

(b) Slade (*loc. cit.*)(c) Kauer *et al.* (*loc. cit.*)

The heat of vaporisation of the isomers indicates that  $\beta$ -isomer has the lowest heat of vaporisation and sublimes easily owing to its symmetrical structure,  $\gamma$  has higher and  $\delta$  has the highest heat of vaporisation due to one and two polar chlorine atoms. The study of the infra-red spectra of the isomers (Daasch, *loc. cit.*) indicates that the  $\beta$ -isomer has the simplest spectra due to its symmetry. The  $\alpha$ -isomer, which belongs to the flexible type, has a complex spectra.

The alkaline dehydrochlorination of the isomers yields a mixture of trichlorobenzenes. The action of alcoholic potash on the hexachlorocyclohexanes is quite distinctive to identify the isomers. The  $\beta$ -isomer is not at all affected by such treatment.  $\alpha$ -Isomer is most readily dehydrochlorinated owing to its flexible nature. Next in the ease of hydrolysis comes the  $\delta$ -isomer which is characterised by two polar chlorine atoms in *para* position, and which is understandable on the basis of the well known *para* linkage in benzene. The  $\gamma$ -isomer is less easily hydrolysed than the  $\delta$  form owing to its single chlorine atom. The resistance to hydrolysis thus increases with the number of peripheral chlorine atoms. The  $\epsilon$ -isomer is less readily hydrolysed than  $\gamma$  owing to the two chlorine atoms in the *ortho* position offering steric hindrance. S. J. Cristal (*J. Amer. Chem. Soc.*, 1947, 69, 339) has suggested a *trans* mode of elimination of HCl as more plausible than the *cis* mode. On this basis  $\delta$ -isomer, which has two *trans* HCl, should be more easily dehydrochlorinated than  $\gamma$ , which has only one *trans* HCl. The behaviour of  $\alpha$ -form can be easily explained as due to its flexible structure, the hydrogen and chlorine atoms can take up the required *trans* positions.

#### *Insecticidal Action of the Isomers*

The toxicity of the four isomers  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  to mosquito larvae and rats has been investigated by Haller and co-workers (*Ind. Eng. Chem.*, 1947, 39, 468) as percentage mortality in certain time. We have calculated the mortality coefficient  $K$  by applying the law of unimolecular reaction,

$$K = \frac{2.3}{t} \log \frac{100}{100 - x}$$



It has been found (Kulkarni, *Ind. J. Mal.*, 1949, 3, 1) that  $K$  is independent of time and concentration. The correlatton between the mortality coefficient and the dipole moment reveals the fact that the dipole moments vary linearly with the logarithm of the mortality coefficient, and that the  $\gamma$ -isomer, which possesses outstanding insecticidal properties, has the highest dipole mement. As however, the  $\epsilon$ -isomer, which is reported to be non-toxic, is likely to have a moment of  $3.6D$ , it appears that the insecticidal property requires a certain optimum electric moment as in the case of the dissociation constants of sulpha compounds.

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INDIAN INSTITUTE OF SCIENCE,  
BANGALORE.

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## A NOTE ON THE ESTIMATION OF ALUMINIUM BY ANTHRANILIC ACID

BY AJITSANKAR BHADURI

Anthranilic acid precipitates aluminium quantitatively as a dense, basic anthranilate. This fact has been utilised for the estimation of aluminium. The precipitate can be easily filtered and washed, and, on ignition, converted into alumina. The precipitation is completed at a  $p_H$  of 4.6. The precipitate is, however, appreciably soluble in sodium acetate solution and also in the presence of much ammonium salts.

The precipitation can be effected either by (A) using sodium anthranilate solution, or by (B) boiling an acid solution of aluminium, containing anthranilic acid, with urea. Ammonia formed by the gradual hydrolysis of urea maintains the  $p_H$  value of the solution between 4.2 and 4.6.

*Method (A).*—A solution of sodium anthranilate was prepared by dissolving anthranilic acid in 100 c.c. of *N*-NaOH solution till the  $p_H$  value of the latter was reduced to 5.4, using Bromocresol green as an indicator.

A solution containing about 0.1 g. of aluminium was neutralised with dilute ammonia till it became slightly turbid. The turbidity was removed by the addition of a very slight excess of dilute hydrochloric acid. The volume of the mixture was made up to 500 c.c., and a requisite quantity of sodium anthranilate solution was added to it till the  $p_H$  became 4.6. Methyl orange was used as an indicator. A white voluminous precipitate was obtained. The mixture was then heated to boiling and afterwards cooled in ice-water. The precipitate was hereafter filtered through a Whatman filter paper No. 40. It was first washed with a solution containing 2 c.c. of the reagent for every 100 c.c. and then several times with cold water to remove the last traces of sodium anthranilate. The precipitate was ignited moist in a platinum crucible and weighed as  $Al_2O_3$ . A solution of chemically pure potash alum was employed for analysis. Some of the results obtained are given below.

TABLE I

Al present.	Wt. of $Al_2O_3$ .	Al found.
0.02043 g.	0.03852 g.	0.02040 g.
0.02043	0.03857	0.02042
0.02452	0.04660	0.02460
0.04086	0.07714	0.04082
0.02043	0.03870	0.02047
0.01684	0.03070	0.01625
0.01021	0.01935	0.01025
0.03064	0.05786	0.03063

*Method (B).*—A solution containing about 0.1g. of aluminium was neutralised with sodium bicarbonate until it turned slightly turbid. The turbidity was removed by the addition of dilute hydrochloric acid in very slight excess. The solution was made up to 500 c.c. and treated with a large excess of anthranilic acid (10-12 equivalents of Al present). Urea (4 g.) was then added to the solution and the mixture was heated to boiling till the precipitation became complete. This usually required more than an hour. The precipitate was allowed to settle in the cold and then filtered and washed as described under (A). Any precipitate adhering to the sides of the beaker was dissolved in a little dilute hydrochloric acid and from the solution aluminium was reprecipitated by the addition of ammonia using Methyl orange as an indicator. This was filtered through a separate small filter paper and washed with a solution of ammonium nitrate (2%). The precipitates were then ignited as described before. The results obtained are given below.

TABLE II

Al present.	Wt. of $\text{Al}_2\text{O}_3$ .	Al found.
0.08752 g.	0.07090 g.	0.08752 g.
0.02258	0.04260	0.02246
0.01876	0.03535	0.01872
0.01876	0.03524	0.01865
0.01876	0.03550	0.01878

It has already been stated that the presence of a large amount of ammonium salts retards the complete precipitation of aluminium. This is apparent from the following results.

TABLE III

$\text{Al}_2\text{O}_3$ present.	Ammonium salt added.	$\text{Al}_2\text{O}_3$ found.
0.01840 g.	$\text{NH}_4\text{Cl}$ 5 g.	0.01180 g.
"	" 2	0.01580
"	" 1	0.01745
"	" 0.8	0.01780
"	" 0.4	0.01850
0.01840	$\text{NH}_4\text{NO}_3$ 2	0.01460
"	" 1	0.01765
"	" 0.8	0.01770
0.01840	$(\text{NH}_4)_2\text{SO}_4$ 1	0.01670

The author's grateful thanks are due to Prof. P. Ray for his kind suggestion and interest.

## A NOTE ON PARACHOR AND RESONANCE

BY W. V. BHAGWAT AND R. P. SHUKLA

No work seems to have been done concerning the relation between parachor and resonance structures of molecules.

Theory of resonance requires that the potential energy of the combination of various possibilities should have a solution with minimum potential energy, so as to give a stability to the molecule. It follows therefore that interchangeable electrons should pass more time in the vicinity of the nuclei, for then alone the potential energy can tend to be minimum. It may therefore be stated that a molecule tends to contract so as to have minimum potential energy or the molar volume, or parachor must tend to decrease. Obviously only such resonance structures of a molecule will be possible as will have parachor values not very different from one another, since resonance requires that the various structures should not have much variation in their potential energies. Resonance therefore from the point of view of parachor requires that (i) the various electronic configurations should have the same or practically the same parachor, and (ii) there should be a tendency to contract and hence the observed parachor should be smaller than the calculated one.

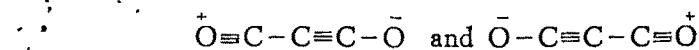
It is interesting to observe that the structural parachor of a triple bond 46.2 is practically double of the value 23.2 for a double bond. Similarly the value of parachor of a double bond is exactly twice the parachor for a four-membered ring. These results are not accidental but highly significant. They satisfy the parachor condition(i) for the resonance to occur.

Further, in conjunction with electron diffraction results, they satisfy the condition (ii), since the bond distance decreases as we pass from single covalent bond to double and triple bond provided that the bond distance between the same two atoms is considered. If this significance were realised earlier, parachor results could have been used to predict the principle of resonance.

The structure of carbon suboxide,  $C_3O_2$ , can be represented as



Hence, according to above parachor consideration, two double bonds can resonate with a triple bond and a single bond, and hence may have the resonating structures :



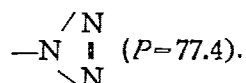
This is confirmed from electron diffraction method, since observed carbon to carbon distance  $1.30\text{\AA}$  and carbon to oxygen distance  $1.20\text{\AA}$  are shorter than the usual interatomic distances required for a double bond.

Similarly carbon dioxide  $O=C=O$  may have the resonance structure  $\bar{O}-C\equiv\bar{O}$  and  $\bar{O}\equiv C-\bar{O}$ . The electron diffraction results indicate  $C-O$  distance equal to  $1.15\text{\AA}$ . The observed value of parachor 775 is smaller than the calculated one 91.2, as required by the hypothesis.

The structure of nitric oxide is best represented as  $\bar{N}=\dot{N}-O$  (Bailey and Cassie, *Phys. Rev.*, 1932, *ii*, 39, 534). It may therefore have the resonating structure  $N\equiv\dot{N}-\bar{O}$ . The zero dipole moment of the molecule and electron diffraction confirm this.

The observed parachor 81.1 is smaller than the calculated value 91.1, as required by our hypothesis.

The structure of hydrazoic acid shows that resonance between the structures  $H-N\leftarrow N\equiv N$  and  $H-N\rightarrow N$  and therefore fulfills the parachor conditions for the existence of resonance. The dipole moment of  $N_3H$  is very small (Shomaker and Spurr, *J. Amer. Chem. Soc.*, 1942, 64, 1184). Azido grouping includes the resonance forms  $-N=N\rightarrow N$  and  $-N\leftarrow N\equiv N$  and this is confirmed from small dipole moment of azides (Bergman and Schutz, *Nature*, 1931, 123, 1077) and from interatomic distances and the heat of formation (Roth and Muller, *Ber.*, 1929, 62, 1190). The parachor value for  $-N_3$  group is found to be 77.2 (Lindman and Thiele, *Ber.*, 1928, 61, 1529; 1930, 63, 702) and apparently corresponds to the structure



The calculated value for the resonating structures  $-N=N\rightarrow N$  and  $N\leftarrow N\equiv N$  is 82.3. Our hypothesis can now explain why the observed value of  $-N_3$  is less than 82.3. It is due to resonance between the structures  $-N=N\rightarrow N$  and  $-N\leftarrow N\equiv N$ , and not due to the cyclic structure as suggested by Lindmann and Thiele (*loc. cit.*)

Aliphatic diazo compounds have the resonance structure  $R_2C=N\rightarrow N$  and  $R_2C\leftarrow N\equiv N$  which is suggested by electron diffraction measurements. However, the parachor shows cyclic structure (Lindmann and Thiele, *loc. cit.*). The low values according to our hypothesis are due to resonance between two straight chain structures and not due to cyclic structure.

The above example clearly shows the significance of the fact that the parachor value of two double bonds is equal to that of a triple bond. Our hypothesis also explains why the observed parachors should be lower than the calculated ones. The results otherwise apparently confirm the structures not supported by dipole moment and electron diffraction measurements.

Carbon bisulphide, like carbon dioxide, should show resonance between the structures  $\bar{S}-C\equiv\bar{S}$ ,  $S=C=S$  and  $\bar{S}\equiv C-\bar{S}$  for the same reason. The observed parachor of  $CS_2$  144, is again less than the calculated one 148.

## STUDIES ON GLASS COMPOSITIONS. A PRELIMINARY NOTE

BY P. SEN

The use of talc as a glass making material in place of sand and lime has been studied.

The effect of magnesia as a glassy constituent has been studied by Turner and his co-workers (*J. Soc. Glass Tech.*, 1919, 3, 275); they found the effect to be beneficial in imparting the properties of chemical durability and lamp-working in preference to lime; but it imparts higher viscosity than lime.

Kühl (*Glashuete*, 1927, 57, 123; *Pottery Gaz.*, 1928, 53, 611) used German dolomite and found that when 4-5% of magnesia was substituted for lime, the resistance of this glass against abrupt changes in temperature was increased. Besborodov (*Keram. Rund.*, 1928, 36, 365) found that substitution up to a maximum of 5.78% of magnesia for lime increased the resistance to sodium carbonate solution and decreased the resistance to hydrochloric acid solution.

With the increasing amount of magnesia, the viscosity, surface tension and difficulty of melting are increased. But Kühl (*Glashuete*, 1933, 63, 371) found that even with the use of magnesia in the form of dolomite, the melting was considerably facilitated when alkalies and lime were simultaneously replaced by barium oxide. The quality of the glass was also improved considerably as it gave increased density, refractive index, hardness and modulus of rupture. This, therefore, gives the clue as to the feasibility of preparing magnesia glasses with proper working properties by substituting lime wholly by some other glass forming oxide. With the advent of the machine operation glasses were required with larger working range and freedom from de-vitrification. Addition of alumina as felspar accomplished these purposes (Ferguson, *Ceram. Ind.*, 1934, 22, 362). There is a general agreement that alumina in glass promotes resistance to thermal and mechanical shocks, imparts lower annealing temperature, and stability against de-vitrification.

All previous workers working with dolomite were faced with the formation of seedy glass and difficulty in firing. Parmelee and Silverman (*Glass Ind.*, 1936, 17, 111) found that addition of alumina decreased the melting rate and the effect decreased with the rising temperature. The total elimination of lime and introduction of alumina generally give rise to  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ , the system which has been studied by Rankin and Merwin (*Amer. J. Sci.*, 1918, 45, 301). This system has binary compounds  $2\text{MgO} \cdot \text{SiO}_2$ ,  $\text{MgO} \cdot \text{SiO}_2$ ,  $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  and a ternary compound  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ , all with lower melting points than  $\text{MgO}$  itself. The refractory character of the individual

oxides and of most of the binary compounds and binary mixtures is no longer evident. The lowest point on the *liquidus* is the eutectic at  $1345^{\circ}$ .

The present work is intended to find out compositions of industrially possible magnesia glass along with felspar which will help working properties. A new source of magnesia was tried, namely Talc. India possesses good deposits of talc and felspar and the work intended may open up a new line in the industrial glass manufacture.

### EXPERIMENTAL

The raw materials used were I. C. I. heavy soda ash, finely ground Indian felspar and talc with the following composition :

TABLE I

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Alkalies	Na <sub>2</sub> CO <sub>3</sub>	Loss	NaCl & Na <sub>2</sub> SO <sub>4</sub>
Felspar	63.83	21.11	0.08	0.21	0.07	13.25	...	0.28	...
Talc	62.1	2.3		2.1	30.2	...	...	3.10	...
Soda ash (I.C.I.)	...	...	...	Trace	Trace	...	96.8	3.10	Trace

Total batch of 100 g. of raw materials was weighed out, mixed in a mortar, shaken thoroughly in a glass jar for about five minutes for thorough mixing and then transferred to a quarter-pound fireclay crucible. The crucibles were placed in an oil-fired furnace and the temperature of melting for each case was observed by means of a Cambridge optical pyrometer and the time for melting noted. The range of compositions taken were: soda ash, 5-25; felspar, 25-75; and talc 10-50 parts by weight with a difference of 5 parts in each case as given in Table II. A rough idea of viscosity of each melt was obtained by drawing rods and by observing the ease of flow of the melt from the crucible.

TABLE II

Series	Melt No.	Soda ash	Felspar	Talc	Melting temp. & time	Observations
A	1	25	65	10	1820° & 4 hours.	Clear melt, light brownish amber colour with no seeds. Highly viscous.
"	2	"	60	15	"	Clear melt, greenish white colour at the centre of the melt. Very viscous.
"	3	"	55	20	"	Clear melt, greenish white in colour with a brownish tinge. No seeds, wires could be drawn. Viscosity lower than Nos. 1 & 2.

## STUDIES ON GLASS COMPOSITIONS

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TABLE II (contd.)

Series.	Melt No.	Soda ash.	Felspar.	Talc.	Melting temp & time.	Observations.
A	4	25	50	25	1820° & 4 hours	Clear greenish white melt; very viscous.
"	5	"	45	30	"	Do.
"	6	"	40	35	"	Do.
"	7	"	35	40	"	Do. Less viscous than Nos. 1-6.
"	8	"	30	45	"	Do. Flowed out of the crucible readily.
"	9	"	25	50	"	Do. Least viscosity in series A.
B	10	20	70	10	"	Clear melt, amber colour with big bubbles. Very difficult to pour out; highly viscous.
"	11	"	65	15	"	Do. Bubble diameter less than No. 10.
"	12	"	60	20	"	Clear melt, greenish white in colour with seeds. Do.
"	13	"	55	25	"	Clear bright melt with seeds. Bubble diameter & viscosity lesser than No. 12.
"	14	"	50	30	"	Clear greenish white melt. Strips and not wires could be drawn. Highly viscous.
"	15	"	45	35	"	Do. Viscosity lower than No. 14.
"	16	"	40	40	"	Do.
"	17	"	35	45	"	Do. Flowed on tilting the crucible. Fluidity more than No. 16, nearly equal to No. 8.
"	18	"	30	50	"	Do. Fluidity more than No. 17. Viscosity is nearly equal to Nos. 8 & 7 of series A.
C	19	15	75	10	"	Light green, semi-melted mass.
"	21	"	65	20	"	Not very clear melt but more clear than No. 19.
"	23	"	55	30	"	Clear greenish white melt with seeds.
"	24	"	50	35	"	Clear melt with greenish smoky in colour.
"	25	"	45	40	"	Clear brownish melt. could not be poured out; viscosity more than series B.
"	26	"	40	45	"	Do.



TABLE II ( *contd.* )

Series	Melt No.	Soda ash.	Felspar.	Talc.	Melting temp & time.	Observations
O	27	15	35	50	1320° & 4 hours	Clear greenish melt, transparency of the glass is more than No. 26. Viscosity more than series B, and practically could not be poured out.
D	28	10	75	15	1400° & 6 hours	Dirty glass
	30	"	65	25	"	Clear green glass. Could not be poured out of the crucible; very viscous.
	32	"	55	35	"	Clear fine melt, greenish in colour. Wire formed with difficulty. Viscosity lesser than No. 30.
"	33	"	50	40	1365° & 4 hours	Do (with seeds).
	34	"	45	45	"	Do. Seeds lesser than No. 33. Wires could be drawn; viscosity lesser than No. 33.
"	35	"	40	50	"	Most clear and transparent melt among series D (Nos. 28-35). Could be poured out of the crucible with difficulty. Seems to be more viscous than series A, B & C.
E	36	5	75	20	1400° & 6 hours	Did not form clear melt.
"	38	"	65	30	"	Do. More clear than No 36.
"	40	"	55	40	"	Clear, greenish white melt. Difficult to flow. Melt full of bubbles.
"	41	"	50	45	"	Melt full of big bubbles.
"	42	"	45	50	"	Clear transparent melt, greenish white in colour. Practically could not be poured out of the crucible. Highest viscosity amongst series A, B, C, D & E.

## DISCUSSION

From the foregoing observations it is evident that

(i) With 5 parts of soda-ash and corresponding parts of felspar and talc, it is impossible to have a workable glass as per melt Nos. 36, 38, 40 and 41.

(ii) With 5 parts of soda ash, 45 of felspar and 50 parts of talc (No. 42) a clear glass is obtained, but due to its high viscosity it is not at all a workable glass. Moreover, they require highest temperature amongst all the glasses formed in the different series.

(ii) With 10 parts of soda ash and with corresponding parts of felspar and talc, clear glasses are obtained except No 28, but the viscosity of the glasses is very high amongst most of the melts.

(iii) With 15 to 25 parts of soda ash and with corresponding parts of felspar and talc, the melts form clear glasses except No 19. As the amount of soda ash decreases below 15, the chance of forming clear glassy melt is decreased.

Hence the workable range of the melts lies between 15 and 20 parts of soda ash.

(iv) Although clear glasses are obtained with felspar ranging from 25 to 75 parts, yet low viscosity melts are only with 25 to 35 parts of felspar.

(v) Talc has a higher fluxing action than felspar and imparts lower viscosity than felspar. In the case of talc, compositions with 10 to 50 parts of talc have melted into clear glasses but those with a higher felspar content are not workable

Substitution of talc for felspar, keeping soda ash constant, gives a more clear and less viscous glass.

### CONCLUSION

The four glasses, Nos. 8, 9, 17 and 18, may be industrially possible glasses which melted between  $1320^{\circ}$  to  $1365^{\circ}\text{C}$ , and have least viscosity amongst the series A, B, C, D and E. These glasses may be utilised for chemical and various other purposes.

Further investigation on the possibilities and properties of these glasses are in progress.

The author's thanks are due to Prof. H. N. Bose for his encouragement, criticism and guidance.

## A NOTE ON THE PREPARATION OF ALKALINE EARTH NITRITES

BY T. M. OZA AND N. L. DIPALI

Preparation of alkaline earth nitrites, particularly of barium nitrite, is important as the latter is used in the preparation of other nitrites. Nitrites of barium, strontium and calcium have been prepared, but the methods used are not adaptable to quick preparation in large amounts. The method has therefore been modified by us to suit these requirements. A further advantage of the modified method lies in yielding the salts in extra pure state.

P. C. Ray (*I. Chem. Soc.*, 1905, 87, 177) prepared pure barium nitrite using molecular proportions of silver nitrite and barium chloride, their saturated solutions in water, mixing, agitating vigorously to coagulate the silver chloride formed, and evaporating the filtrate nearly to dryness on a water-bath. The nitrite thus prepared was found by us to contain traces of nitrate which persisted even after two recrystallisations. This is presumably formed by autoxidation of the nitrite during evaporation of the large bulk of the solution; silver nitrite is very sparingly soluble in water.

To reduce the bulk of the solution we have substituted water by ammonia, diluted half with water, as the solvent for silver nitrite. To the concentrated solution of silver nitrite in such ammonia, a solution of the alkaline earth chloride in water is added, the mixture agitated and the ammonia then boiled off. The dissolved nitrite is then recovered either by evaporation in a desiccator or by treatment with alcohol. The analyses of the nitrites of calcium, strontium and barium, prepared by this method, are given below. The strontium and calcium nitrite did not part with their water of crystallisation even on intensive desiccation.

*Calcium nitrite*: 0.0750 g. and 0.0878 g. gave respectively 0.0668 g. and 0.0804 g.  $\text{CaSO}_4$ . [Found: Ca, 0.01968 g. and 0.02362 g. respectively *i.e.*, 26.23% and 26.91%. Calc. for  $\text{Ca}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ : Ca, 26.66%].

0.0685 g. and 0.0412 g. of the substance consumed 41.5 c.c. and 25.0 c.c. of 0.05N- $\text{KMnO}_4$ . [Found:  $\text{NO}_2'$ , 61.25% and 61.35% respectively. Calc. for  $\text{Ca}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ :  $\text{NO}_2'$ , 61.3%].

*Strontium nitrite*: 0.1133 g. and 0.0924 g. gave 0.1056 g. and 0.0862 g. of  $\text{SrSO}_4$ . [Found: Sr, 0.05037 g. and 0.04111 g. respectively, *i.e.*, 44.46% and 44.49%. Calc. for  $\text{Sr}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ : Sr, 44.32%].

0.0225 g. and 0.0280 g. of the substance consumed 4.575 c.c. and 5.725 c.c. of 0.1002N- $\text{KMnO}_4$ . [Found:  $\text{NO}_2'$ , 0.01054 g. and 0.01319 g. respectively, *i.e.*, 46.85% and 47.11%. Calc. for  $\text{Sr}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ :  $\text{NO}_2'$ , 46.56%].

*Barium nitrite*: 2.386 g. gave 2.2104 g. anhydrous substance. Loss per 229 g.  $\text{Ba}(\text{NO}_2)_2$  would therefore be 18.19 g. *i.e.*, one molecule water; 0.1997 g. and 0.1811 g. of anhydrous substance gave 0.2028 g. and 0.1845 g.  $\text{BaSO}_4$ . [Found: Ba, 0.1194 g. and 0.1086 g. respectively, *i.e.*, 59.77% and 59.98%. Calc. for  $\text{Ba}(\text{NO}_2)_2$ : Ba, 59.89%].

0.0899 g. and 0.0602 g. of the substance consumed 15.80 c.c., and 10.65 c.c., of 0.09951N- $\text{KMnO}_4$ . [Found:  $\text{NO}_2$ , 0.03616 g. and 0.02438 g. respectively, *i.e.*, 40.23% and 40.5%. Calc. for  $\text{Ba}(\text{NO}_2)_2$ :  $\text{NO}_2$ , 40.11%].

Thanks of the authors are due to Mr. V. T. Oza for preparing calcium nitrite and verifying the analysis.

CHEMISTRY DEPARTMENTS,  
GUJARAT COLLEGE, AHMEDABAD  
AND  
KARNATAK COLLEGE, DHARWAR.

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## REVIEWS

**Frontiers in Chemistry, Vol. 8 : Frontiers in Colloid Chemistry.**—Edited By R. E. Burk and Oliver Grummitt. Published by Interscience Publishers, Inc., New York and London, under the auspices of Western Reserve University. 1950. Pp. 156+vi. Price \$ 4.00.

The contributors to this publication are authorities in their respective subjects. The subject of colloid science is making rapid progress in its different aspects and the publication of this present Volume dealing with the recent developments of some of the most important branches of colloid science will be welcome.

Chapter I deals with the role of adsorption in colloid science written by Hugh Taylor. The Brunauer-Emmett-Teller theory of multimolecular adsorption, and all its recent modifications have been fully discussed. In chapter II H. H. Strain has discussed the theory and technique of chromatographic adsorption analysis. This type of analysis, first described in 1906 by the Russian botanist, Tswett, is now very widely applied for the resolution of mixtures into all their components and quantitative recovery. The procedure in three steps—adsorption of the mixture of solutes in the upper portions of the column, development of the chromatogram by a flow of fresh solvent, and liberation of the components separately by means of special solvents—has been fully discussed, as also the many precautions which must be observed during such analysis.

The applications of synthetic resin in ion-exchanges have lately been very wide and their manifold uses for such purposes as softening and deionization of water, recovery of valuable electrolytes in dilute solutions and removal of undesirable heavy metals from organic solvents, are well known. Proper utilisation of these synthetic resins needs a careful study of their ion-exchange reactions. Robert Meyers has very thoroughly dealt with this topic, in the light of recent investigations.

In chapter IV Domerall has discussed the sedimentation of giant molecules and colloidal particles as also larger particles, by various ultracentrifuge methods. The techniques have been described at length.

Contributions of McBain on the behaviour of colloidal electrolytes are well known and the two interesting chapters on the subject will be very much welcomed by the readers. The properties and characterisation of colloidal electrolytes have been discussed and their distinction from strong electrolytes have been pointed out. Typical conductivity data for the strong electrolytes hydrochloric acid as compared with the Debye-Hückel-Onsager slope and as contrasted with potassium laurate and lauryl sulphonic acid, undecylsulphonic acid, myristylsulphonic acid and cetyl sulphonic acid have been given. At extreme dilution all conform more or less to the theoretical Debye-Hückel-Onsager slope. Thereafter the equivalent conductivity of the colloidal electro-

lyte becomes far less, passes through a very distinct minimum and then rises again. The behaviour of solution has also been discussed in details.

The get-up of the book is excellent. It should be very useful to all advanced students and research workers of chemistry in general and of colloid science in particular.

S. P. R.

**Electron Microscopy.**—By Ralph W. G. Wyckoff. Published by Interscience Publishers, Inc., New York, 1949. Pp. 248. Price 30/-sh.

This book deals with the technique of electron micrography and its various uses and no attempt has been made to incorporate in it the details of theoretical discussions regarding the various components of the electron microscope. Evidently, this volume is intended for those who want to start some work with an electron microscope of commercial type. A few such commercial electron microscopes have been described briefly in the second chapter and in the next chapter the methods of adjusting the various parts of the instrument have been explained elaborately. Chapter IV deals with the method of preparation of the specimens for electron micrographs and in the next chapter the principle of the metal shadowing of small objects for visualization has been explained and the methods of metal shadowing have been described and a few such micrographs have been described with the help of illustrations. In chapter VI various uses of both photo micrographs and electron micrographs of surface replicas have been described and a few such micrographs have been reproduced. In chapter VII the usefulness of the study of electron micrographs of suspension of many objects which are themselves big enough to be visible under optical microscopes has been explained and a few such micrographs reproduced in this chapter are very interesting. The next chapter deals with electron micrographs of viruses. The photographs reproduced are extremely instructive to bio-physicists. In the last two chapters the methods of photographing macromolecules and studying their structures with the help of an electron microscope have been discussed briefly with the help of illustrations.

There are altogether 20 beautiful illustrations in the book and each chapter, besides including such illustrations, is followed by an up-to-date bibliography. Hence it is an useful book of reference to all research workers who are using electron microscopes for any purpose. The book is printed on art paper and the get-up leaves nothing to be desired.

S. C. S.

**Technique of Organic Chemistry, Vol. I. Physical Methods of Organic Chemistry, Parts I and II.**—Edited by Arnold Weissberger. Second Edition. Published by Interscience Publishers, Inc., New York & London. Pages 1084 and 1036 Price \$ 12. 50 per part.

The book represents a compilation of the various physical methods employed in the laboratory. The second edition consists of the following

chapters in Part I: Temperature measurement; Temperature control; Determination of melting and freezing temperatures; Determination of boiling and condensation temperatures; Determination of vapor pressure; Determination of density; Determination of solubility; Determination of viscosity; Determination of surface and interfacial tension, parachor; Determination of properties of Monolayers and Duplex films; Determination of osmotic pressure; Determination of diffusivity; Determination with ultracentrifuge; Calorimetry; Microscopy; Determination of crystal form; and Crystallochemical analysis.

Part II contains X-Ray diffraction; Electron diffraction; Refractometry; Spectroscopy and spectrophotometry; Colorimetry, photometric analysis; Fluorimetry and Turbidimetry; Polarimetry; Determination of dipole moments; Conductometry; Electrophoresis; Potentiometry; Polarography; Determination of magnetic susceptibility; Determination of radioactivity; and Mass spectrometry.

In this edition five new chapters, namely I, II, V, XIII & XXVI have been added; chapters VIII, IX, XII, XXIV, XXX & XXXI have been rewritten; other chapters have been thoroughly revised and in some of them new material incorporated. In the preface to the first edition the editor pointed out "It has been the object of the authors to provide a description of the tested methods, the theoretical background for understanding and handling them, and the information necessary for critical evaluation of experimental results." In our opinion the authors have been, generally, quite successful towards this end. In fact, this book has become a companion in most of the important laboratories in America. Although the book was primarily meant for the organic chemist, physical chemist, polymer chemist, biologist and other research workers dealing with organic chemical problems, have found these volumes to be very useful.

Addition of new material and rectification of defects of the first edition, have made this edition all the more useful. The authors also appear to have made every attempt to supply up-to-date information. Evidently a book dealing with so many subjects is not expected to be an exhaustive source of information. The demands of the more sophisticated reader in any particular branch, however, have been met to a considerable extent by the inclusion of a carefully prepared bibliography at the end of each chapter.

P. B.

**Organic Chlorine Compounds.**—By Ernest H. Huntress Published by John Wiley & Sons Inc., New York, 1948. Pp. 1443. Price \$ 27.50.

In this book a summary of data of organic chlorine compounds of the Order 3 has been compiled in a rational and conveniently usable form. No less than 1320 compounds have been listed in this inventory and a summary of their methods of preparation, properties, chemical behaviour, physical

constants has been given. Industrial aspects of important compounds have been dealt with. Industrial aspects of important compounds have been properly emphasised. Literature references are thorough and exhaustive and include patent literature as well. In view of the recent large-scale industrial application of organic chlorine compounds Prof. Huntress by this monumental publication has indeed rendered a great service to chemists interested in this field.

P. C. M.

**An Introduction to Organic Chemistry.**—By Roger J. Williams and Lewis F. Hatch. Published by D. Van Nostrand Company Inc., 1948. Pp. 668. Price \$4.75.

The book is intended to serve as an elementary text for the beginners and is quite suitable for undergraduates who had no previous training in the subject. The author has presented the basic principles of Organic Chemistry in a remarkably clear and lucid style that will acquaint the readers with the most important descriptive material and also a theoretical interpretation of the phenomena studied. It does not, however, provide sufficiently broad or critical treatment for use as a text beyond the elementary stage.

The material has been systematically arranged with 22 Chapters devoted to the study of aliphatic compounds, including amino-acids, proteins, carbohydrates and cycloparaffins, as well as terpenes and camphors. Of the remaining, 15 Chapters include a treatment of aromatic and heterocyclic compounds, dyestuffs and alkaloids. One chapter has been devoted to Organic Compounds of special biochemical interest e. g., vitamins, hormones, antibiotics, and another to a general introduction of the special physicochemical methods largely used in Organic Chemistry including tracer element technique. In addition, brief reference to modern detergents, high polymers, synthetic rubber, weed killers, insecticides has been included. The utilisation of petroleum as a source of various aliphatic and aromatic compounds has been prominently indicated. Principles of modern electronic theory of valency and resonance have been introduced in a manner quite in keeping with such an elementary text.

For its judicious selection of up-to-date information and clarity of expression the book is highly suitable for undergraduate and medical students.

P. C. M.

**Synthetic Methods of Organic Chemistry, Vol. II.**—By W. Theitheimer. Published by Interscience Publishers ; Inc., New York, 1949 Pp. 324. Price \$ 7. 50.

This is the first English edition of the author's "Synthetische methoden der organischen Chemie, Reportorium II" published in 1948. And English edition of Volume I has already been published. In the series of volumes to be published regularly under this project, the author intends to catalog recent



applications of classical methods as well as fundamental new approaches developed for the synthesis of organic compounds. In the volume under review the methods published in Swiss, French and British journals during the years 1945-46 have been described. Collection of materials from other foreign journals, particularly American, was not possible due to wartime restrictions when such journals were not available in Switzerland. These papers will be included in a subsequent volume.

The book is primarily intended to be a reference volume that "should provide a quick survey of the situation in hand and obviate the necessity of first searching the entire literature". A wealth of practical information is placed at the disposal of the laboratory workers and abstracts contain sufficient details to be of immediate value in actual laboratory applications. The literature references are exhaustive and in many cases refer not only to the particular paper concerned but also to other publications.

To organise such a unwieldy subject matter in a systematic manner is indeed a difficult task. To meet this challenge, the author has adopted Weygand's System of classifying reactions according to the nature of the bond formed. One unfamiliar with this system of classification may initially experience some difficulty in consulting this book. For this purpose the system of classification and reaction symbols used have been illustrated lucidly with typical examples in the Introduction of the book. The exhaustive subject index where the common trivial names and notations have been employed might help to overcome the initial difficulties.

Supported by Beilstein's "Handbuch der organischen Chemie" these volumes will provide invaluable guide to synthetic organic chemists engaged in academic and industrial research and as such should find a place in every library and laboratory. There can be little doubt that subsequent publications in this series will find a warmer welcome from every laboratory.

P. C. M.

**A Century of British Chemistry.**—By Dr F. Sherwood Taylor. Published for the British Council by Longman Green and Co. First published 1947. Pp 40+11 plates.

This work surveys in brief the principal achievements of British Chemists in different fields of Chemistry during the past 100 years. The book is divided into six chapters under the following headings :—

(1) The theory of valency, (2) Gases, Liquids and Solids, (3) Colloid Science and Surface Chemistry, (4) Chemical kinetics, (5) Inorganic Chemistry (6) Organic Chemistry.

This book will be useful to those who are interested in the history of the development of Chemistry with special respect to the contributions made by the British Chemists.

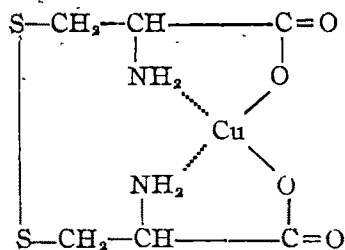
M. N. G.

# CYSTIN AS AN ANALYTICAL REAGENT. ESTIMATION OF COPPER, CADMIUM, COBALT, NICKEL AND ZINC; AND THEIR SEPARATION FROM CALCIUM, BARIUM AND MAGNESIUM

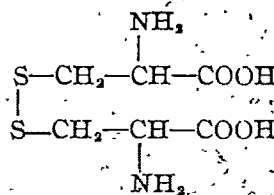
By PRIYADARANJAN RÂY AND AJITSANKAR BHADURI

Cystin has been used as an analytical reagent with satisfactory results for the estimation of copper, cadmium, cobalt, nickel and zinc, as well as for the separation of the latter three elements from calcium, barium and magnesium. Attempt to separate zinc from iron and aluminium in the presence of tartaric or sulphosalicylic acid in ammoniacal solution led, however, to no fruitful results. The precipitation of zinc under these circumstances was considerably retarded, or even more or less completely inhibited, depending upon the amount of iron or of sulphosalicylic acid present, though tartaric acid or sulphosalicylic acid alone has got no effect.

Cystin is known to form a bright blue, silky, crystalline copper compound, resembling copper glycine. This is insoluble in water and belongs obviously to the class of inner metallic complex salts like the latter. Its structure can, therefore, be represented by the planar square configuration as given below :



Copper cystin.



Cystin.

An insoluble cadmium compound of cystin has also been described. It was therefore considered desirable to explore the possibility of its usefulness as an analytical reagent. Cystin has now been found to react also with cobalt, nickel and zinc salts under suitable conditions to form insoluble compounds; and methods have been developed for the estimation of all these elements, as well as of copper and cadmium, in the form of their cystin salts. The reagent has also been found to give useful results in the separation of cobalt, nickel and zinc from the alkaline earths and magnesium. On the other hand, though iron or aluminium does not react with cystin, it has not been found possible to separate zinc from them even in the presence of masking reagents like tartaric acid or sulphosalicylic acid, which are known to form soluble complexes with these elements.

Cystin is sparingly soluble in water and in all common organic solvents, but dissolves in dilute mineral acids and ammonia. The reagent was therefore used in dilute HCl solution. Strong acids, however, decompose cystin with liberation of  $\text{H}_2\text{S}$ . An 1% solution of cystin in normal (1-N) hydrochloric acid was employed in the present work.

## E X P E R I M E N T A L

*Estimation of Copper*

For the preparation of copper cystin a solution of cystin in dilute hydrochloric acid was added in slight excess to an acidified solution of copper sulphate. The mixture was heated to boiling and treated with dilute ammonia till it smelt of the latter. The bright blue, silky precipitate was allowed to settle on the water-bath, filtered and washed with hot slightly ammoniacal water till free from cystin. The precipitate was then washed with absolute alcohol and finally with anhydrous ether. The product was afterwards kept in a sulphuric acid desiccator for about half an hour. The substance is soluble in excess of ammonia and also in dilute acids.

Copper was estimated volumetrically after decomposition of the substance with fuming nitric acid. [Found : Cu, 19.86, 19.95.  $\text{Cu}(\text{C}_6\text{H}_{10}\text{N}_2\text{S}_2\text{O}_4) \cdot \text{H}_2\text{O}$  requires Cu, 19.89 per cent].

*Procedure.*—The solution, containing about 0.1 g. of copper, was diluted to 250 c.c. and heated to boiling. To the hot solution about 40 c.c. of the reagent (1% cystin in *N*-HCl) were added. The mixture was then treated with ammonia, drop by drop, till it became distinctly alkaline, when the copper cystin separated completely in the form of a bright blue, silky crystalline precipitate. This was allowed to stand on the water-bath and then filtered in a tared asbestos-based Gooch crucible. The precipitate was washed with hot ammoniacal water until free from cystin. Usually 5 to 6 washings were enough. It was then washed three times with absolute alcohol and finally thrice with anhydrous ether on the pump. The crucible with the precipitate was afterwards kept in a sulphuric acid desiccator for half an hour and then immediately weighed. The weight of copper was calculated from the formula given above. Cu = 19.89%. The results are collected in Table I.

TABLE I

Cu present.	Cu-cystin.	Cu found.	Cu present.	Cu-cystin.	Cu found.
0.03258 g.	0.1639 g.	0.03260 g.	0.04402 g.	0.2201 g.	0.04377 g.
0.02671	0.1339	0.02664	0.05509	0.2760	0.05489
0.01460	0.0729	0.01450	0.00881	0.0446	0.00887
0.02086	0.1047	0.02083	0.0207	0.0104	0.00207
0.03111	0.1564	0.03111	0.00103	0.0052	0.00103

*Estimation of Cadmium*

Cadmium cystin was precipitated in the same way as the copper compound. This was washed with hot ammoniacal water till free from cystin and then with hot distilled water. The fine white, silky precipitate was afterwards dried at a temperature of  $150^\circ$  to a constant weight. [Found : Cd, 32.10, 32.06.  $\text{Cd}(\text{C}_6\text{H}_{10}\text{N}_2\text{S}_2\text{O}_4)$  requires Cd, 32.07 per cent].

*Procedure.*—The silky white precipitate of cadmium cystin, obtained as described above, was filtered on a tared asbestos Gooch, washed with hot water containing a little ammonia (1%) until free from cystin, and dried to a constant weight at 105°. Cd = 32.07%. Table II gives the results obtained.

TABLE II

Cd present.	Cd-cystin.	Cd found.	Cd present.	Cd-cystin.	Cd found.
0.09038 g.	0.2839 g.	0.09103 g.	0.03882 g.	0.1210 g.	0.03880 g.
0.07764	0.2423	0.07770	0.01354	0.0423	0.01356
0.06470	0.2016	0.06464	0.01971	0.0613	0.01966
0.05176	0.1616	0.05181	0.00986	0.0307	0.00984
0.05307	0.1655	0.05305	0.00657	0.0205	0.00657

#### *Estimation of Cobalt*

Cobalt cystin was prepared in the same way as the corresponding copper or cadmium compound. An excess of cystin was used in order to prevent any precipitation of cobalt hydroxide by ammonia. An excess of ammonia should be avoided. The light pink coloured precipitate was allowed to settle by keeping it on the water-bath. This was filtered, washed at first by decantation with hot 1% ammonia solution till free from cystin and then with hot water. The precipitate was finally washed with absolute alcohol, followed by anhydrous ether, and then left for about 30 minutes in a desiccator over  $\text{H}_2\text{SO}_4$  before being weighed. [Found: Co, 18.72.  $\text{Co}(\text{C}_6\text{H}_{10}\text{N}_4\text{S}_2\text{O}_4) \cdot \text{H}_2\text{O}$  requires Co, 18.71 per cent].

Table III gives the results obtained.

TABLE III

Co present.	Co-cystin.	Co found.	Co present.	Co-cystin.	Co found.
0.02486 g.	0.1331 g.	0.02490 g.	0.01591 g.	0.0851 g.	0.01592 g.
0.02188	0.1172	0.02188	0.01492	0.0798	0.01495
0.02088	0.1116	0.02085	0.00249	0.0133	0.00249
0.01989	0.1064	0.01990	0.00995	0.0532	0.00996
0.01790	0.0957	0.01790	0.00119	0.0063	0.00118
0.01642	0.0878	0.01643	0.00099	0.0053	0.00099

Cobalt can be easily separated from Ca, Ba or Mg by this method. Ammonia employed for precipitation should, however, be freshly prepared to avoid the formation of carbonate. Some of the results obtained are given in Table IV.

In the presence of magnesium, cobalt was precipitated by cystin after the addition of some ammonium chloride to prevent the precipitation of magnesium hydroxide. The precipitate of cobalt cystin was dissolved in a little dilute hydrochloric acid and

the cobalt was reprecipitated from the solution by cystin following the usual procedure. Nevertheless, the results indicate a slight absorption of magnesium by the cobalt precipitate. In the filtrate from cobalt cystin calcium was estimated volumetrically after precipitation as oxalate. Barium was estimated gravimetrically as  $\text{BaSO}_4$ , and magnesium as  $\text{Mg}_2\text{P}_2\text{O}_7$ .

TABLE IV

Metal present.	Cobalt cystin	Metal found.	Metal present	Cobalt cystin	Metal found.
Co, 0.00995 g	0.0532 g.	0.00996 g.	Co, 0.01989 g.	0.1065 g.	0.01992 g.
Ca, 0.02164			Ba, 0.01310		0.01310
Co, 0.00995	0.0534	0.00999	Co, 0.00995	0.0536	0.01003
Ca, 0.03246		0.03234	Mg, 0.01665		0.01650
Co, 0.01989	0.1063	0.01988	Co, 0.00995	0.0539	0.01009
Ca, 0.01082			Mg, 0.04995		0.04962
Co, 0.00995	0.0533	0.00998	Co, 0.01989	0.1063	0.01988
Ba, 0.03930			Mg, 0.01665		
Co, 0.00995	0.0534	0.01000	Co, 0.01989	0.1077	0.02014
Ba, 0.01310			Mg, 0.06660		
Co, 0.00995	0.0534	0.01000	Co, 0.02984	0.1619	0.03019
Ba, 0.02620			Mg, 0.08325		

#### Estimation of Nickel

Nickel was estimated by following the procedure prescribed for cadmium. The light green precipitate of nickel cystin was dried at  $105^\circ$ . [Found: Ni, 18.68.  $\text{Ni}(\text{C}_6\text{H}_{10}\text{N}_2\text{S}_2\text{O}_4) \cdot \text{H}_2\text{O}$  requires Ni, 18.65 per cent].

The results are given in Table V.

TABLE V

Nickel present.	Ni-cystin	Ni found	Nickel present	Ni-cystin	Ni found.
0.03786 g.	0.2025 g.	0.03780 g.	0.01578 g.	0.0848 g.	0.01582 g.
0.02525	0.1356	0.02527	0.01052	0.0564	0.01053
0.02610	0.1399	0.02610	0.00210	0.0113	0.00210
0.02104	0.1127	0.02102	0.00105	0.0056	0.00105

Nickel was separated from calcium, barium and magnesium by precipitation with cystin using freshly prepared carbonate-free ammonia. The results are collected in Table VI.

TABLE VI

Metal present.	Nickel cystin.	Metal found.	Metal present.	Nickel cystin.	Metal found
Ni, 0.01052 g. Ca, 0.01082	0.0562 g.	0.01048 g.	Ni, 0.02104 g. Ba, 0.01310	0.1143 g.	0.02132 g. 0.01307
Ni, 0.01052 Ca, 0.02164	0.0567	0.01058	Ni, 0.02104 Ba, 0.02620	0.1131	0.02109
Ni, 0.01052 Ca, 0.03246	0.0565	0.01053	Ni, 0.02104 Ba, 0.03930	0.1129	0.02106
Ni, 0.02104 Ca, 0.02164	0.1121	0.02091	Ni, 0.01052 Mg, 0.03330	0.0567	0.01058
Ni, 0.02104 Ca, 0.01082	0.1144	0.02134 0.01094	Ni, 0.01052 Mg, 0.04995	0.0563	0.01050
Ni, 0.01052 Ba, 0.02620	0.0564	0.01053 0.02616	Ni, 0.01052 Mg, 0.01665	0.0562	0.01049 0.01676
Ni, 0.01052 Ba, 0.03930	0.0563	0.01051	Ni, 0.02104 Mg, 0.03330	0.1128	0.02104
			Ni, 0.03156 Mg, 0.04995	0.1688	0.03150

Calcium, barium and magnesium were estimated as stated before.

#### Estimation of Zinc.

Zinc cystin was obtained as a milky white precipitate following the procedure described under cadmium. The precipitate was dried at  $105^{\circ}$ – $110^{\circ}$ . The precipitate is fairly soluble in ammonia in presence of ammonium salts. [Found: Zn, 21.56.  $\text{Zn}(\text{C}_6\text{H}_{10}\text{N}_4\text{S}_2\text{O}_4)$  requires Zn, 21.55 per cent]. Table VII shows the results obtained.

TABLE VII

Zn present.	Zn-cystin.	Zn found.	Zn present.	Zn-cystin.	Zn found.
0.03351 g.	0.1560 g.	0.03359 g.	0.01675 g.	0.0777 g.	0.01674 g.
0.02345	0.1089	0.02346	0.01117	0.0519	0.01118
0.02234	0.1035	0.02230	0.00559	0.0258	0.00555
0.02011	0.0932	0.02009	0.00223	0.0102	0.00221

Zinc was separated from calcium, barium and magnesium by precipitation with cystin. The excess acid in the solution in all these cases was first neutralised with sodium bicarbonate prior to the addition of ammonia. Results are given in Table VIII.

TABLE VIII

Metal present.	Zn-cystin.	Metal found.	Metal present.	Zn-cystin.	Metal found.
Zn, 0.01061 g. Ca, 0.01082	0.0491 g.	0.01059 g.	Zn, 0.01051 g. Ba, 0.01310	0.0488 g.	0.01050 g.
Zn, 0.01061 Ca, 0.02164	0.0492	0.01060 0.02164	Zn, 0.01061 Ba, 0.03930	0.0491	0.01059
Zn, 0.01061 Ca, 0.03246	0.0492	0.01068	Zn, 0.02122 Ba, 0.01310	0.0983	0.02120
Zn, 0.02122 Ca, 0.01082	0.0982	0.02116	Zn, 0.02122 Ba, 0.02620	0.0983	0.02120
Zn, 0.02122 Cr, 0.02164	0.0982	0.02116	Zn, 0.02122 Ba, 0.0393	0.0983	0.02118
Zn, 0.02122 Ca, 0.03246	0.0985	0.02122 0.03232	Zn, 0.01061 Mg, 0.04995	0.0492	0.01060
Zn, 0.01061 Ba, 0.02620	0.0492	0.01060 0.02607	Zn, 0.02122 Mg, 0.01665	0.0985	0.02122 0.01674
			Zn, 0.02122 Mg, 3.03330 or 0.04995	0.0983	0.02119

Calcium, barium and magnesium were estimated as in the previous cases.

An attempt to separate zinc from iron in presence of alkaline tartrates led to no fruitful results. It was found that though tartaric acid even in large excess had no effect on the precipitation of zinc by cystin, presence of iron, however, considerably retarded its precipitation. With a large excess of iron no precipitation of zinc occurred at all. This is apparent from the results collected in Table IX below.

TABLE IX

Zinc present = 0.01147 g.			
Fe added.	Rochelle salt added.	Zn-cystin.	Zn found.
	2 g.	0.05185 g.	0.01117 g.
	5	0.05187	0.01118
	10	0.05180	0.01116
	20	0.05178	0.01116
0.00433 g.	5	0.05115	0.01105
0.00816	"	0.04517	0.00973
0.01298	"	0.03976	0.00857
0.02597	"	0.02216	0.00478
0.04328	.	No precipitation	

Similar results were obtained in an attempt to separate zinc as zinc cystin from iron and aluminium in presence of sulphosalicylic acid which is known to form complexes with the latter metals. But as these complexes break up at the boiling temperature, the precipitation of zinc was carried out in all these cases by heating the mixture on the water-bath only, to prevent any possible separation of the hydroxides of iron and aluminium. Table X gives some results of such estimations. Like tartaric acid, sulphosalicylic acid itself has got no effect on the precipitation of zinc by cystin in alkaline medium. The solution in all these cases was neutralised with  $\text{NaHCO}_3$  before the addition of ammonia for precipitating zinc. This was to prevent the formation of much ammonium salts which tended to keep the zinc cystin in solution.

TABLE X

Zinc present = 0.01064 g.

Fe or Al.	Sulphosalicylic acid.	Reagent.	Zn-cystin.	Zn found.
—	2.5 g.	Slight excess	0.04944 g.	0.01065 g.
—	4.0	„	0.04952	0.01067
—	5.0	„	0.04960	0.01069
Fe, 0.04435 g.	5.0	0.10 g.	0.03692	0.00706
„	4.0	„	0.04422	0.00953
„	3.0	„	0.04597	0.00987
„	2.0	„	Fe(OH) <sub>3</sub> co-precipited.	
„	2.5	0.20	0.04917	0.01060
„	„	0.18	0.04926	0.01062
„	„	0.15	0.04795	0.01034
0.0887	5.0	0.20	0.03687	0.00795
„	„	0.30	0.04170	0.00898
„	„	0.40	0.04760	0.01026
„	„	0.45	0.04918	0.01060
Al, 0.02490	1.0	0.10	0.04424	0.00953
„	„	0.12	0.04574	0.00986
„	„	0.15	0.04759	0.01026
„	„	0.18	0.04952	0.01067
0.0497	2.0	0.20	0.04504	0.00970
„	„	0.25	0.04964	0.01070



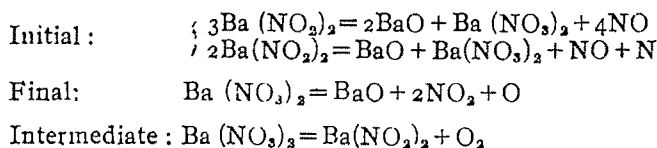


## THE THERMAL DECOMPOSITION OF MAGNESIUM NITRITE

BY TRAMBAKLAL M. OZA AND N. L. DIPALI

In the study of the mechanism of the reactions taking place in the decomposition of nitrites by heat, magnesium nitrite offers special interest as it decomposes almost completely below 200°, so that the extent of complications due to side reactions coming in at higher temperatures is, with this substance very small. Pure magnesium nitrite has been prepared by a method not used previously in its preparation and the substance has been decomposed under various conditions with a view to affording an insight into the nature of the solid residue at various stages during the course of the decomposition. The gaseous products consist of nitrous anhydride, nitric oxide and nitrogen; the amounts of nitrogen are, at times, quite negligible and at any rate never exceed 2 to 3% in any experiment. The solid residue contains nitrite, nitrate and oxide and its composition tends to the proportion nitrite used up to nitrate formed to oxide produced as 3 : 1 : 2. The stages involved in the reaction have been clearly brought out.

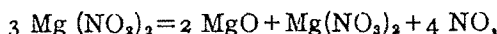
The thermal decomposition of nitrites was studied by P. C. Ray (*J. Chem. Soc.*, 1905, 87, 177), who found the presence of the oxide and the nitrate of the metal, in addition to the undecomposed nitrite, in the residue and nitric oxide, nitrogen peroxide and nitrogen in the gaseous products of the decomposition. The amount of nitrogen peroxide was small, while as regards the relative proportions of nitrogen formed by different nitrites, it is stated that "calcium and magnesium nitrites yielded very little pure nitrogen whereas the barium and sodium salts gave considerable amounts". The following mechanism was assigned to the reactions taking place :



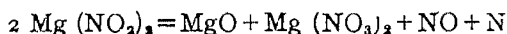
That he was not completely satisfied with the mechanism is significant in the following statement: "as a matter of fact, several reactions go on side by side, some of which, again, probably overlap so that no sharp line of demarcation can be laid down between them". The concluding remarks of the paper are still more significant: "As a result of the purely thermal decomposition, a portion of the salts breaks up into the peroxide and nitric oxide but as the former is unstable, specially under diminished pressure, at the temperature at which the scission takes place, it parts with its oxygen both to the nitric oxide and also to the undecomposed salt in a state of fusion, and that it is in this way that internal oxidation and reduction are brought about". The evidence before the present worker (Oza and Shah, *J. Univ. Bom.*, 1942, 70; Oza, this *Journal*, 1945, 22, 173; Oza and Walavalkar, *ibid.*, 1945, 22, 243), as also that brought forward in this paper, is a testimony to exactness of vision and foresight of the great chemist.

In the thermal decomposition of magnesium nitrite, studied by Ray and Ganguli (Ray, *loc. cit.*), the general nature of the reactions was said to be identical with the above.

It was noticed that the decomposition started as early as 60° in vacuum, and further that perceptible amounts of nitrous fumes were seen at the very outset of the experiments. On the basis of their analytical data they concluded that by far the greater proportion of the nitrite decomposed as

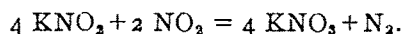


but they felt strongly inclined to ascribe the following reaction,

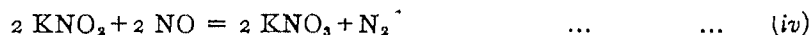


to explain the equivalent amounts of oxide and nitrate in the residue and the appearance of nitrogen in the gas.

Ostwald (*Annalen*, 1914, 403, 32) studied the thermal decomposition of alkali nitrite and advanced the view that nitrogen was formed by the action of nitrogen tetroxide on the fused nitrite as



Oza and Shah (*loc. cit.*) felt inclined to this view but Oza (*loc. cit.*) and Oza and Walavalkar (*loc. cit.*), who undertook a careful study of the thermal decomposition of alkali nitrites at low temperature, at which the intermediate and final stages of Ray's reaction may be largely inoperative, showed that the initial stage,  $2 \text{ KNO}_2 \rightleftharpoons \text{K}_2\text{O} + \text{NO} + \text{NO}_2$  (Oza and Shah, *loc. cit.*) was followed by reactions producing nitrogen and the latter was produced by the action of nitric oxide and *not* nitrogen peroxide on the fused nitrite. The following mechanism was ascribed:



It was also shown that the reactions mostly occurred in the molten phase though the possibility of reaction (iv) occurring at the gas-liquid interface was not precluded.

It may be observed that the conclusions of Oza and co-workers differ in two important respects from those of the previous workers, viz., (i) the initial stage as consisting of the dissociation of the nitrite into oxide, nitric oxide and nitrogen tetroxide and (ii) the formation of nitrogen as dependent on the action of nitric oxide on the fused nitrite, nitrogen peroxide *not* producing nitrogen in contact with the fused nitrite in *one* step. These conclusions have been arrived at by studying the nature and proportion of the gaseous products and the residue at various stages in the course of the decomposition as also by the study of the action of nitric oxide and oxygen on the nitrites in the fused state, the experiments having been conducted near the fusion temperature of the nitrites with a view to eliminating, as far as possible, complications in the reactions. Magnesium nitrite offers, from this point of view, a unique substance as it decomposes at a very low temperature and produces very little nitrogen (Ray and Ganguli, *loc. cit.*), so that the nitrogen-producing reactions are practically absent. This substance was therefore supposed to supply important information on the nature of the stages concerned before the production of nitrogen occurred.

In the present work magnesium nitrite has been prepared by a method not hitherto used in its preparation and the pure substance has been used in experiments in which the nitrite is decomposed under differing conditions of experiment. The gaseous products of the decomposition, as also the solid residue left at the end of each experiment, have been analysed. The results have been found to be very illuminating, as in addition to suggesting the nature of the stages involved, they show that the mechanism may be of quite a universal character in the case of all nitrites.

### EXPERIMENTAL

*Preparation of Magnesium Nitrite.*—Magnesium nitrite was prepared by Lang (*Svenska Akad. Handl.*, 1860, 3, 14), Hampe (*Annalen*, 1863, 128, 337), Spiegel (*Chem Ztg.*, 1894, 18, 1423) and P. C. Ray (*loc. cit.*). Various methods were tried by us e.g., double decomposition with equimolecular quantities of silver nitrite and magnesium chloride, followed by evaporation of the filtrate in an air-oven at 50°; the nitrite obtained was of very poor quality containing less than 30% substance; no nitrite was found in the precipitate when ammoniacal solution of the nitrite was used; equimolecular quantities of barium nitrite and magnesium sulphate were dissolved separately in water, mixed and the filtrate dehydrated over  $P_2O_5$ . The solid, dried to a constant weight, contained (i) 73.52% and (ii) 73.08%  $Mg(NO_2)_2$ , the  $Mg(NO_2)_2$  content of  $Mg(NO_2)_2 \cdot 2H_2O$  being 76.4%

The method employed by us was that made use of by Ray (*J. Chem. Soc.*, 1907, 91, 2031) in the preparation of double nitrites. This enabled us to dispense with the previous step, preparation of pure barium nitrite. Equimolecular quantities of silver nitrite and magnesium chloride were made into a paste in a clean mortar and the extract, which had the deep tint of very concentrated nitrite solutions, was concentrated further to a syrupy state in a  $P_2O_5$  desiccator under partial vacuum and then dried to a constant weight in the desiccator under the ordinary pressure. The substance thus obtained gave on analysis the following results:

(i) 0.0914 g. and 0.0828 g. of the substance gave respectively 0.0712 g. and 0.0642 g.  $MgSO_4$  (Treadwell and Hall, Vol. II, 6th Ed., p. 76). [Found: Mg, 0.01438 g. and 0.01297 g. i.e., 15.74% and 15.66% respectively. Calc. for  $Mg(NO_2)_2 \cdot 2H_2O$ : Mg, 15.98%].

(ii) 0.0396 g. and 0.0414 g. of the substance consumed 10.65 c.c. and 11.15 c.c. of 0.09709N- $KMnO_4$  respectively. [Found:  $Mg(NO_2)_2$ , 0.0308 g. and 0.03148 g. i.e., 75.95% and 76.03% respectively. Calc. for  $Mg(NO_2)_2 \cdot 2H_2O$ :  $Mg(NO_2)_2$ , 76.4%]. Ray (*loc. cit.*) observed that the stable variety of magnesium nitrite contained two molecules of water of crystallisation.

*Apparatus and Procedure.*—The apparatus consisted of a tube, A, closed at one end and fitted with a ground-in-glass joint at the other through which it was connected to a bubbler, B, through another ground-in-glass joint. The bubbler was connected through another ground-in-glass joint to the sprengel and hyvac pumps.

A weighed quantity of magnesium nitrite was taken in A and about 2 c.c. of a freshly made, concentrated solution of potassium hydroxide was placed in B. The apparatus was set up with a coating of vacuum grease on all the joints and taps and then evacuated with the hyvac pump. The apparatus was tested for leaks by allowing it to stand for a few hours, and if vacuum-tight, the sprengel pump was worked with its characteristic clicks for half an hour before the start of an experiment.

An oil-bath was heated outside to the temperature of the experiment and then inserted below A. Temperature was maintained to within about  $\pm 2^\circ$  by regulating the flame under the bath. After the heating for the stipulated time was over, the bath was removed and the gases were pumped off into eudiometers and kept aside for analysis. The residue in A was dissolved out in distilled water and made to 100 c.c. in a measuring flask and subsequently examined for its nitrite and nitrate content. The alkali in B was also made to 100 c.c. and was examined for nitrite alone as the gas was found to contain always a large excess of free nitric oxide, and the alkali was therefore not likely to contain any nitrate.

*Analysis of Gaseous products and Residues.*—The gas, measured out at the room temperature and pressure, was absorbed in alkaline sodium sulphite, the end of the absorption being tested with acidified ferrous sulphate. The residual gas was taken as nitrogen. All volumes, recorded in the tables, are at N.T.P.

For determining nitrous anhydride, the alkali solution (25 c.c.) was treated with 10 c.c. of 0.025 *N*-KMnO<sub>4</sub> solution to which dilute sulphuric acid was then added.

TABLE I

*Heating a fixed mass of magnesium nitrite at various temperatures for 30 mins.*

1 Expt. No.	2 Wt. Mg(NO <sub>2</sub> ) <sub>2</sub> · 2H <sub>2</sub> O taken.	3 Wt. anhyd. Mg(NO <sub>2</sub> ) <sub>2</sub> corresp. to column 2.	4 Temp	5 Composition of gaseous products			
				Total	N <sub>2</sub> O <sub>3</sub>	NO.	N <sub>2</sub>
1	0.2486 g	0.1898 g.	110°	6.4 c.c.	0.85 c.c.	5.45 c.c.	0.1 c.c.
2	0.2498	0.1907	130°	43.85	1.8	41.25	0.8
3	0.2474	0.1891	150°	46.05	2.3	42.85	0.9
4	0.2460	0.1878	170°	44.86	1.65	42.51	0.7
5	0.2744	0.2096	190°	46.97	2.01	44.20	0.8
6 Composition of the residue.			7 Mg(NO <sub>2</sub> ) <sub>2</sub> used up	8 Composition in g. mols			
Nitrite.	Nitrate.	Oxide (calc.)		Nitrite used up.	Nitrate produced.	Oxide formed.	9 Ratio NO <sub>2</sub> ': NO <sub>3</sub> ': O".
0.1515 g.	0.0238 g.	0.006813 g.	0.0383 g.	$3.3 \times 10^{-4}$	$1.6 \times 10^{-4}$	$1.68 \times 10^{-4}$	2 : 1 : 1
0.01483	0.06937	0.04222	0.1758	$1.5 \times 10^{-3}$	$0.469 \times 10^{-3}$	$1.05 \times 10^{-3}$	3 : 1 : 2
0.01164	0.06476	0.04403	0.1771	$1.52 \times 10^{-3}$	$0.436 \times 10^{-3}$	$1.09 \times 10^{-3}$	
0.00868	0.06648	0.04414	0.1791	$1.6 \times 10^{-3}$	$0.589 \times 10^{-3}$	$1.03 \times 10^{-3}$	
0.01008	0.08586	0.04568	0.1995	$1.7 \times 10^{-3}$	$0.578 \times 10^{-3}$	$1.14 \times 10^{-3}$	3 : 1 : 2

The mixture was well shaken and heated to about  $70^{\circ}$ . The excess of the permanganate was then reduced by adding a known volume of a standard (0.025 *N*) tetroxalate solution and the excess of the latter was then titrated back with the standard  $\text{KMnO}_4$  solution.

Nitrite in the solid residue was determined in the manner detailed above with the difference that 0.1 *N* solutions were used. For determining nitrate in the residue, the nitrite present was first oxidised to nitrate by adding the requisite amount of standard  $\text{KMnO}_4$  (0.1 *N*) solution and the total nitrate then determined by the ferrous sulphate method (Cumming and Kay, "Quantitative Chemical Analysis", 6th Ed., pp. 100-101). The magnesium oxide, present in the residue, was worked out by subtracting the magnesium equivalent of magnesium nitrite and magnesium nitrate found from that of the magnesium nitrite taken at the start of the experiment.

Table I contains the results of experiments carried out with a fixed mass of magnesium nitrite, heated at different fixed temperatures for a fixed period of time. The results show that (i) nitrogen trioxide, nitric oxide and nitrogen are, all, produced at all temperatures between  $110^{\circ}$  and  $190^{\circ}$ ; (ii) the amount of nitrogen is very small at  $110^{\circ}$  and its amount is not more than 2.5% of the total gas even at  $190^{\circ}$ ; the proportion of nitrous anhydride,  $\text{N}_2\text{O}_3$ , is at low temperatures ( $110^{\circ}$ ) as high as 13% but diminishes rapidly with rise of temperature; nitric oxide is the main gaseous product of the decomposition, its proportion being normally not less than 80%; (iii) magnesium oxide and magnesium nitrate are always present along with magnesium nitrite in all experiments, and it appears peculiar that the amount of decomposition, in half-an-hour, is the same at  $130^{\circ}$  and at  $190^{\circ}$ , although at the latter temperature the rate of the decomposition is much greater showing that beyond a certain stage appreciable amounts of the nitrite do not apparently decompose: the amounts of it formed and decomposed, in a given unit or interval of time, may not be very much different from each other; (iv) in all the experiments except the first, wherein the extent of the decomposition is but slight, the proportions of nitrite used up to nitrate produced, to oxide formed, are approximately as 3 : 1 : 2; in the first experiment these are as 2 : 1 : 1.

TABLE II

*Effect of time on the decomposition of a fixed mass of magnesium nitrite, heated at  $110^{\circ}$ .*

1 Expt No	2 Wt. of $\text{Mg}(\text{NO}_2)_2$ , $2\text{H}_2\text{O}$ taken.	3 Wt. anhyd. $\text{Mg}(\text{NO}_2)_2$ corresp. to column 2.	4 Time.	5 Composition of gaseous products.			
				Total.	$\text{N}_2\text{O}_3$ .	NO.	$\text{N}_2$ .
1	0.2486 gr.	0.1898 g.	30 min.	6.4 c.c.	0.85 c.c.	5.45 c.c.	0.1 c.c.
2	0.2528	0.1930	60	21.22	0.88	19.5	0.84
3	0.2442	0.1864	90	22.15	1.55	20.2	0.4
4	0.2678	0.2046	90	22.3	1.3	20.6	0.4
5	0.2530	0.1932	120	25.3	0.9	24.2	0.2
6	0.2712	0.2071	120	25.1	1.1	23.5	0.5

TABLE II (contd.)

6 Composition of the residue			7	8 Composition in g. mols.			9 Ratio
Nitrite.	Nitrate.	Oxide (calc.)	Mg (NO <sub>2</sub> ) <sub>2</sub> used up.	Nitrite used up.	Nitrate produced.	Oxide formed.	NO <sub>2</sub> : NO <sub>3</sub> : O <sup>*</sup> .
0.1515 g	0.0238 g	0.006813 g	0.0383 g.	$3.3 \times 10^{-4}$	$1.6 \times 10^{-1}$	$1.68 \times 10^{-4}$	2 : 1 : 1
0.09550	0.040	0.02221	0.0975	$8.4 \times 10^{-4}$	$4.0 \times 10^{-4}$	$5.5 \times 10^{-4}$	
0.08429	0.0502	0.02183	0.1021	$8.6 \times 10^{-4}$	$3.4 \times 10^{-4}$	$5.4 \times 10^{-4}$	2.5 : 1 : 1.5
0.09718	0.0540	0.02227	0.1074	$9.2 \times 10^{-4}$	$3.7 \times 10^{-4}$	$5.5 \times 10^{-4}$	2.5 : 1 : 1.5
0.08123	0.0536	0.02433	0.1120	$9.6 \times 10^{-4}$	$3.6 \times 10^{-4}$	$5.7 \times 10^{-4}$	2.5 : 1 : 1.5
0.09361	0.0525	0.02493	0.1135	$9.78 \times 10^{-4}$	$3.54 \times 10^{-4}$	$5.8 \times 10^{-4}$	

Table II contains results of the experiments with a fixed mass of magnesium nitrite, heated at 110° for varying periods of time. It may be observed in these results that the effect of time is not so great between 60 and 90 minutes or between 60 and 120 minutes as between 30 and 60 minutes, showing again, as before, that beyond a certain stage the net amount of magnesium nitrite apparently decomposing is very small. The results in Table II show further that (i) nitrous anhydride, nitric oxide and nitrogen are all present in the gaseous products of the decomposition, the amount of nitrogen present being never greater than 1 to 2%; the proportion of nitric oxide present is large and compares favourably with that in the preceding table; the amounts of nitrous anhydride do not increase proportionately with time, being practically the same in 30 as in 120 minutes; (ii) as in the preceding set of experiments, magnesium oxide and magnesium nitrate are both present in the residue along with magnesium nitrite; the proportion of magnesium nitrite used up to magnesium nitrate formed, to magnesium oxide produced is approximately as 2.5 : 1 : 1.5 and a tendency is visible for these proportions to become as 3 : 1 : 2; (iii) as before, the net quantity of magnesium nitrite decomposing in experiments of longer duration are comparatively small with respect to those in experiments of shorter duration.

Results of the experiments on the effect of variation of mass of magnesium nitrite at a constant temperature (110°), heated for a fixed interval of time (30 mins.) are recorded in Table III. These results show that (i) practically no nitrogen is present, almost all the gas consisting of nitrous anhydride and nitric oxide; amounts of nitrous anhydride, though small, are much larger than those in the preceding tables and fluctuate, the proportion being as large as 16% with 0.62 g of magnesium nitrite. This observation, along with the corresponding observations made in Tables I and II, shows that (i) the presence of nitrous anhydride in the gas is due mainly to the small portion which escapes the sphere of reaction at the commencement of the experiment; (ii) the effect of increasing mass is to increase the amount of the decomposition, in almost a regular manner; (iii) as usual, magnesium oxide and magnesium nitrate are both present in the residue along with magnesium nitrite; the proportion of magnesium nitrate is, it must be particularly observed, very small in the first experiment and the proportions of magnesium nitrite used up and magnesium oxide formed are approximately equal to each other. With increase in mass, the proportions of magnesium oxide and magnesium nitrate tend to become identical and the proportion of magnesium nitrite used up

TABLE III

*Effect of mass on the decomposition of magnesium nitrite at 110° for 30 mins.*

1	2	3	4	5		
Expt. No.	Mg(NO <sub>2</sub> ) <sub>2</sub> , 2H <sub>2</sub> O taken	Anhydrous Mg(NO <sub>2</sub> ) <sub>2</sub> corresp. to column 2.	Total gas	Composition of gaseous products:		
				N <sub>2</sub> O <sub>3</sub>	NO	N <sub>2</sub> .
1	0.1248 g.	0.0952 <sup>5</sup> g	2.45 c.c.	0.36 c.c.	2.06 c.c.	Trace
2	0.2486	0.1948 g	6.4	0.85	5.45	0.1 c.c.
3	0.3780	0.2885	9.2	0.98	8.21	Trace
4	0.5002	0.3819	15.42	2.1	13.2	0.12.
5	0.5116	0.3907	15.39	1.86	13.2	0.3
6	0.6270	0.4782	20.2	3.2	16.55	0.4

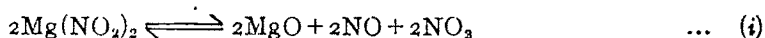
6			7	8			9
Composition of the residue.			Mg(NO <sub>3</sub> ) <sub>2</sub> used up.	Composition in g. mols.			Ratio. NO <sub>2</sub> : NO <sub>3</sub> : O'.
Nitrite.	Nitrate.	Oxide (calc.)		Nitrite used up.	Nitrate produced	Oxide formed.	
0.07603 g.	0.0038 g.	0.001877 g.	0.01923 g	$1.7 \times 10^{-4}$	$2.6 \times 10^{-5}$	$1.4 \times 10^{-4}$	6:1:5
0.1515	0.0238	0.006813	0.0383	$3.3 \times 10^{-4}$	$1.6 \times 10^{-4}$	$1.68 \times 10^{-4}$	2:1:1
0.2211	0.0456	0.01109	0.0574	$6.7 \times 10^{-4}$	$3.1 \times 10^{-4}$	$3.5 \times 10^{-4}$	2:1:1
0.2795	0.0544	0.01804	0.1024	$9.3 \times 10^{-4}$	$4.4 \times 10^{-4}$	$4.9 \times 10^{-4}$	2:1:1
0.2880	0.0675	0.01744	0.1027	$9.4 \times 10^{-4}$	$4.56 \times 10^{-4}$	$4.68 \times 10^{-4}$	2:1:1
0.3529	0.0802	0.01951	0.1183	$10.2 \times 10^{-4}$	$5.42 \times 10^{-4}$	$4.77 \times 10^{-4}$	

becomes almost twice as great as that of the nitrate formed or oxide produced; (iv) magnesium nitrite and nitric oxide are both present amongst the products, in all these experiments, in plentiful amounts and still no nitrogen is found in the gas.

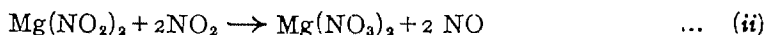
The outstanding fact about all these experimental results is that in all cases where the decomposition has reached a steady state, the proportions of magnesium nitrite used up to magnesium nitrate formed, to magnesium oxide produced are, as nearly as possible, 3 : 1 : 2, while in other cases where the decomposition has presumably not reached such a state, the proportions are fluctuating and may be 2.5:1:1.5 or 2:1:1 or some such as these. In any case, there is significantly a distinct tendency for the latter figures to pass into the former (Table II).

## DISCUSSION

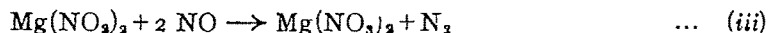
The results in Tables I, II and III show that magnesium nitrite dissociates in the initial stage as



This is soon followed by the reaction between the produced nitrogen tetroxide (of the nitrous anhydride: nitric oxide and nitrogen tetroxide being produced in equivalent amounts) and the unchanged nitrite in the decomposing mass as



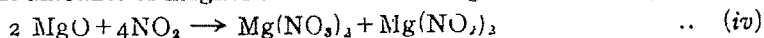
and, to a very meagre extent, by the reaction



The extent of the reaction (iii), though very trifling, seems to depend upon temperature.

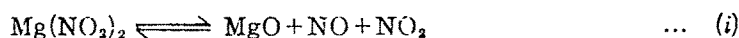


As magnesium oxide begins to be formed and accumulate in the residual mass, a reaction seems to come into being consuming a portion of the oxide and producing, in the process, equivalent amounts of magnesium nitrite and magnesium nitrate, as



Reaction (iv) is very prominent in the later stages when the proportion of free magnesium oxide present in the residue is considerable.

The fact that nitrogen is almost entirely absent in all experiments at  $110^\circ$ , even when the extent of the decomposition is fairly appreciable, shows that nitrogen is not produced in the initial stage. This fact, taken together with the fact that nitrous anhydride is present in all experiments, favours the view that the initial stage in the decomposition of magnesium nitrite consists, as in the case of alkali nitrites (Oza, *loc. cit.*), of the dissociation of the nitrite as



This equation requires that nitric oxide and nitrogen tetroxide should be present in equivalent amounts. In practice, this is never found and in view of the well known properties of nitrogen tetroxide, it can hardly be expected. Nitrogen is known to be a very strong oxidising agent and reacts at ordinary temperatures, and even at temperatures at and below zero very vigorously with all substances with which it comes into contact. Its slight appearance in these experiments must therefore be ascribed not to its less than 100% activity but to its escape, immediately after formation, into the highly vacuous space above by distension rendered possible by the comparatively low activity of magnesium nitrite and by the absence of magnesium oxide in the sphere of its influence, viz., the decomposing mass. The facts that (i) the proportion of nitrous anhydride is much greater in half hour experiments than in experiments of greater duration and (ii) the proportion of nitrous anhydride is almost the same in all experiments in Tables I and II, and (iii) the proportion of nitrous anhydride depends upon the mass of the nitrite undergoing the decomposition, being greater with greater mass, provide evidence in favour of the conception. It is thus evident that the nitrogen peroxide reacts, immediately after its formation, in a manner which produces nitric oxide, the gas found in large amounts in the gaseous products, but not nitrogen. Under the conditions of the experiments this would occur as in the reaction (ii).

It is also evident that the reaction (ii) follows reaction (i) and is not simultaneous with the latter; the comparatively very low value of nitrate in the first of the mass experiments (Table III) is an evidence in favour of this view.

Another side reaction bringing about the consumption of the nitrogen tetroxide seems to set in as soon as magnesium oxide is produced in the decomposing mass. The very nature of it requires that it cannot set in before the reaction (i) and, that, it sets in, though to a very limited extent, as soon as the decomposition begins, i.e., as soon as magnesium oxide is produced in the reacting mass. Magnesium oxide seems to fix up nitrogen peroxide (or tetroxide) quite effectively and practically none of the tetroxide can escape unreacted if magnesium oxide is present in the residue in sufficient amounts. The observation that the amount of nitrogen tetroxide in the gas is large in all half-hour experiments at  $110^\circ$  seems dependent on two factors, viz lack of magne

sium oxide in the decomposing mass at the start of the experiments and distension of some of the gas in the vacuum prevailing in the system at the commencement of the experiments.

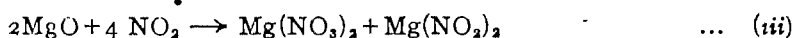
With a view to obtaining a more correct idea of the role of magnesium oxide in the decomposition, an experiment was performed in which about 20% (on the weight of magnesium nitrite taken) magnesium oxide was admixed with the magnesium nitrite. The heating was done for half an hour at  $130^{\circ}$ . The results of this experiment are given below and show that free nitrous anhydride is present in the gas to a much smaller extent (cf. expt. 2, Table I). It should be noticed also that the decomposition is retarded by the presence of magnesium oxide, a product of the decomposition or dissociation in the system and this observation is interesting as it lends evidence to the reversible nature of the commencing stage as shown in equation (i) above. Note may also be taken of the facts that (a) the amount and proportion of nitrogen in the gas is much less in this experiment than in the corresponding experiment of the temperature series; (b) the amounts of magnesium nitrite used up to magnesium nitrate formed, to magnesium oxide produced are almost strictly in the ratio of 3:1:2. This shows that when conditions become favourable for the complete consumption of all the nitrogen tetroxide of the nitrous anhydride, disengaged in the decomposition, the solid residue is likely to show the amount of magnesium nitrite (used up) to magnesium nitrate formed to magnesium oxide produced in the ratio of 3:1:2.

$\text{Mg}(\text{NO}_2)_2$ , $2\text{H}_2\text{O}$ taken.	Wt. $\text{Mg}(\text{NO}_2)_2$ + $\text{MgO}$ taken.	Anhydrous $\text{Mg}(\text{NO}_2)_2$ .	Total.	Composition of the gaseous products:		
				$\text{N}_2\text{O}_3$ .	$\text{NO}$ .	$\text{N}_2$ .
0.2616 g.	0.3270 g.	0.1998 g.	34.4 c.c.	1.24 c.c.	32.9 c.c.	0.25 c.c.

Residue: Composition			Mag. nitrite	Composition in g. mols.			
Nitrite.	Nitrate formed.	Oxide produced.	used up.	Nitrite used up	Nitrate formed.	Oxide produced	Ratio $\text{NO}_2:\text{NO}_3:\text{O}^{\circ}$ .
0.04391 g.	0.06547 g.	0.03607 g.	0.1599 g.	$13.44 \times 10^{-4}$	$4.42 \times 10^{-4}$	$9.016 \times 10^{-4}$	3:1:2

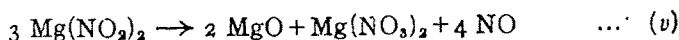
Nitrogen peroxide will react with magnesium oxide evidently as



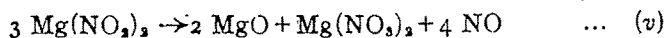
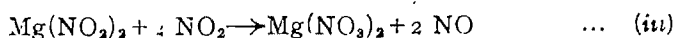
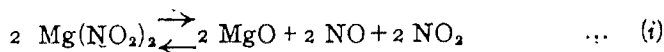
producing equivalent quantities of the nitrite and the nitrate. The extents to which the reactions (ii) and (iii) occur, depend on the nature of the decomposing mass and on the conditions, viz., temperature, mass, etc., prevailing in the experiment. It is this production and consumption of magnesium oxide and magnesium nitrite, during the course of the decomposition, which modify the relative amounts of magnesium nitrite, magnesium oxide and magnesium nitrate observed, and account for the fluctuations in the amounts of these substances observed in the experiments.

It is now possible to account for the relative proportions, 3:1:2, of the magnesium nitrite used up to magnesium nitrate formed, to magnesium oxide produced, found in all the experiments which have run to completion and also to account for the pro-

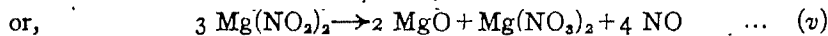
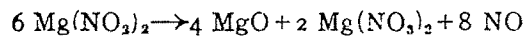
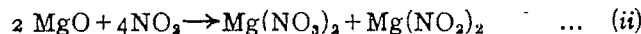
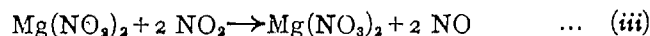
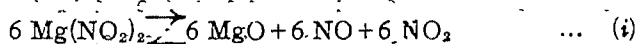
portions, other than these, observed in the experiments recorded in Tables I, II, and III. The initial stage, represented by the equation (i), is modified, in the commencing stages of the decomposition, mainly by the reaction put down in the equation (ii), in the intermediate stages of the decomposition, mainly by the reactions represented by the equations (iii) and (iv), and in the end stages of the decomposition, mainly by the reaction represented by the equation (v). It can be readily shown that the different stages acting cumulatively, will produce the result represented by the equation,



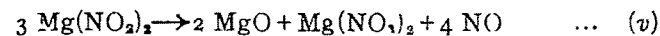
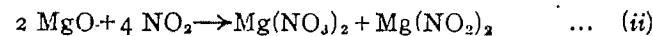
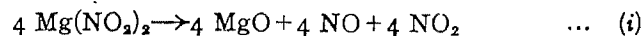
Thus, in the commencing stages:



in the intermediate stages:



in the end stages:

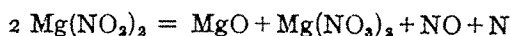


The experimental results show that nitrogen is produced in all the experiments without exception. The proportion of nitrogen, though very small, is found to depend upon the temperature of the experiment and it is evident that it is produced as the result of a reaction that is going on concurrently with the others. As its proportion is very small, it cannot affect, to any appreciable extent, the course of the main reactions under the conditions of the experiments.

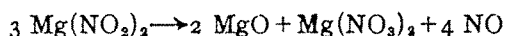
Although the temperature used in these experiments precludes the possibility of reduction of nitric oxide, the production of nitrogen must, at any rate, be ascribed to the reaction,

$\text{Mg}(\text{NO}_2)_2 + 2 \text{NO} = \text{Mg}(\text{NO}_3)_2 + \text{N}_2$  (cf. Oza, *loc. cit.* Oza and Walavalkar, *loc. cit.*). This is readily understood when it is remembered that the extent of a reaction is conditioned also by the *state* of the reacting molecules and that Maxwellian distribution renders it probable that, at any temperature, a certain fraction of the reacting molecules, the fraction may be very small, may by deriving energy from the molecules with which they happen to collide, become excited and capable of reacting.

To account for the occurrence of nitrogen Ray and Ganguli (*loc. cit.*) suggested the reaction,



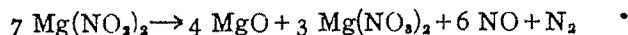
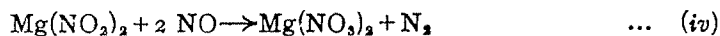
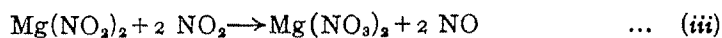
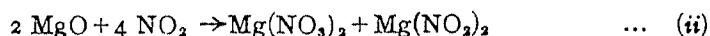
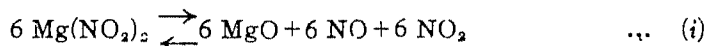
and this equation had, from their point of view, the additional merit that it accounted for the equivalent amounts of magnesium nitrate and magnesium oxide observed by them in their residue. They were, however, disinclined to ascribe the equation to the mechanism as the amount of nitrogen observed by them did not agree with its requirements. They therefore put forward the equation,



which is the same as the equation (v), given above. From their point of view, this equation had, on the other hand, the defect that it did not account for the production of nitrogen and for the occurrence of equivalent amounts of nitrate and oxide found by them in the residue of their experiment.

The present work shows that their observation on the equivalence of magnesium nitrate and magnesium oxide in the residue is only incidental or casual (*vide expts. in Table III and Expt. 1, Table I*). It is not possible to account for the quantity of nitrogen observed by them in their experiment. The present work shows that the amount of nitrogen never exceeds 2.5% and therefore the 12.5%, found by them, cannot be explained except on the assumption that their operative temperature might have been higher. With the temperatures used by us (up to  $190^\circ$ ), the proportion has not been found to exceed 2.5%; to be sure of this fact, an experiment was performed in which about 0.5 g. of magnesium nitrite was heated at  $130^\circ$  (their temperature was  $120^\circ$ ) till about 100 c.c. gas was given off. Analysis of this gas too showed the presence of only 2.0 c.c. nitrogen in the total of 93.8 c.c. which contained, in addition, 89.0 c.c. nitric oxide and 2.8 c.c. nitrous anhydride.

The way in which the production of nitrogen will modify the relative proportions of magnesium nitrite used up to magnesium nitrate formed, to magnesium oxide produced, may be demonstrated by equations in an arbitrary case:



The volume of nitrogen, as shown in this last equation, is one-sixth of that of nitric oxide and the proportions of the nitrite used up to the nitrate formed, to the oxide produced are, roughly as 2:1:1.

THE M. R. SCIENCE INSTITUTE,  
GUJARAT COLLEGE, AHMEDABAD  
AND  
THE KARNATAK COLLEGE, DHARWAR

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CIS AND TRANS ISOMERISM OF  $\beta$ -ARYLGLUTACONIC ACIDS AND  
THEIR DERIVATIVES. PART I. FORMATION OF THE  
CIS AND TRANS FORMS OF  $\beta$ -COUMARYL-3- $\beta$ -  
(4-METHOXYPHENYL)-ACRYLIC ACID

By V. M. BHAVE

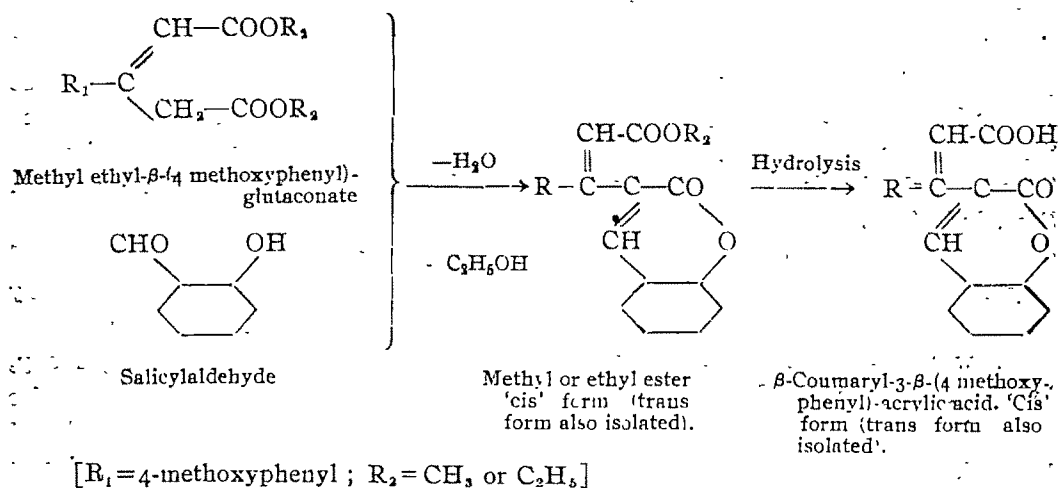
$\beta$ -Arylglutaconic acids and their derivatives are ordinarily known to exist in the *cis* form. If, however, the esters of these acids are condensed with salicylaldehyde, which contains a hydroxy group, using piperidine as the condensing agent,  $\beta$ -coumaryl-3- $\beta$ -arylacrylic acid and their esters are obtained in *cis* and *trans* modifications. The present paper deals with the results obtained in the case of  $\beta$ -(4-methoxyphenyl)-,  $\beta$ -(4-methoxy-3 methylphenyl)-,  $\beta$ -(2-methoxy-5 methylphenyl)-,  $\beta$ -(2-methoxy-4 methylphenyl)- and  $\beta$ -(4-methoxy-2 methyl-5 isopropylphenyl)-glutaconic acids.

Dibasic acids containing a double bond are well known to exhibit *cis* and *trans* isomerism as illustrated by the example of maleic and fumaric acids. Substituted and unsubstituted glutaconic acids, which also contain a double bond, might therefore be expected to exist in every case in distinct *cis* and *trans* modifications. But it was found by Perkin and Tattersall (*J. Chem. Soc.*, 1905, 87, 361) that although alkyl substituted glutaconic acids could be readily obtained in the *cis* and *trans* forms, the simple unsubstituted glutaconic acid existed only in one form. In the case of  $\beta$ -aryl-substituted glutaconic acids, Thorpe and Bland tried to prepare the *cis* and *trans* forms of  $\beta$ -phenylglutaconic acid, but without success. They observed, however, that when the symmetry of the glutaconic acid molecule was destroyed, as in the case of the semianilides of these acids, these derivatives could be obtained in well defined *cis* and *trans* modifications (Thorpe and Bland, *ibid.*, 1912, 101, 862). Before 1931 very few  $\beta$ -aryl-substituted glutaconic acids were known. But after the development of a new method for the preparation of these acids by Limaye and co-workers, several workers have reported the formation of various  $\beta$ -aryl-substituted glutaconic acids and many of their derivatives (Limaye *et al.*, this *Journal*, 1931, 8, 139, 798; *J. Univ. Bom.*, 1934, part II, 140; Gogte, *Proc. Ind. Acad. Sci.*, 1934, 1A, 59 *et seq.*). But in all these cases the  $\beta$ -aryl substituted glutaconic acids, and also their derivatives including semianilides have been reported only in one form, which is obviously the *cis* modification, since the above acids readily yield their anhydrides and the derivatives are then prepared from the anhydrides.

It was therefore considered interesting to study the methods and conditions, if any, by which the *trans* modifications of  $\beta$ -arylglutaconic acids or their derivatives could also be obtained. Since the simple semianilides of these acids had already been prepared and were reported only in one form, although their molecules were unsymmetrical, it was thought worthwhile to prepare and study other derivatives of these acids containing unsymmetrical molecules. As  $\beta$ -(4-methoxyphenyl)-glutaconic acid could be prepared readily, it was first selected for this study.

By replacing one of the reactive hydrogen atoms of ethyl  $\beta$ -(4-methoxyphenyl)-glutaconate by a methyl group, followed by hydrolysis,  $\beta$ -(4-methoxyphenyl)- $\alpha$ -methyl-

glutaconic acid was prepared. Though its molecule is unsymmetrical, this acid is found to exist in the *cis* form only as it gives its anhydride (Limaye and Bhavé; *Rasayanam*, 1939, 1, 178). Then by the condensation of ethyl  $\beta$ -(4-methoxyphenyl)-glutaconate with benzaldehyde in the presence of sodium ethoxide, followed by hydrolysis,  $\alpha$ -benzal- $\beta$ -(4-methoxyphenyl)-glutaconic acid was prepared (Limaye and Bhavé, *loc. cit.*). This again was obtained only in the *cis* form, since it readily gave its anhydride. Thus, it appears that mere symmetrical or unsymmetrical nature of the molecule is not sufficient to ensure that both *cis* and *trans* forms will be formed and isolated. In addition to the unsymmetrical nature of the molecule a new factor, viz., the presence of a hydroxy group in the substituent, has now been introduced by condensing ethyl  $\beta$ -(4-methoxyphenyl)-glutaconate with salicylaldehyde instead of benzaldehyde, in the presence of piperidine. The condensation took place after boiling the alcoholic solution for ten hours. From the reaction mixture in this case, however, two isomeric ethyl esters of the empirical formula  $C_{21}H_{18}O_5$  were obtained in almost equal amounts. One of the esters melted at  $165^\circ$ , while the other at  $127^\circ$ . It was also found that if instead of ethyl ester the methyl ester of the glutaconic acid were employed for the condensation, two isomeric methyl esters of empirical formula  $C_{20}H_{16}O_5$ , one melting at  $163^\circ$  and other at  $147^\circ$ , were obtained. On hydrolysis, both these pairs of isomeric methyl and ethyl esters gave rise respectively to two isomeric acids, one melting at  $213^\circ$  and the other at  $198^\circ$ . Titration results and analysis have shown that both the acids are monobasic and have the formula  $C_{16}H_{14}O_6$ . By analogy with the formation of the *cis*- $\alpha$ -benzal- $\beta$ -arylglutaconic acid, mentioned above, and taking into account the results of analysis and combustion, the formation of these esters and acids could be represented by the following scheme with the difference that in this case every compound was obtained in two isomeric forms:—



Since there is no other possibility of formation of isomeric acids of this formula in the condensation, the above acids and esters can be represented as the *cis* and *trans* forms of  $\beta$ -coumaryl-3- $\beta$ -(4-methoxyphenyl)-acrylic acid and their esters. Further evidence in support of this view was obtained when it was found that by the action of

concentrated sulphuric acid one of the two acids, viz., the acid of m.p.  $213^{\circ}$ , could be almost quantitatively converted into the other isomeric acid of m.p.  $198^{\circ}$ , although the reverse change could not be brought about.

The above reaction is found to be of general application and similar *cis* and *trans* forms of the methyl and ethyl esters and of the corresponding substituted acrylic acids can be obtained by condensing the ethyl and methyl esters of the other known  $\beta$ -arylglutaconic acids with salicylaldehyde in the presence of piperidine. The results obtained in the case of the esters of

- (i)  $\beta$ -(4-methoxy-3-methylphenyl)-glutaconic acid,
  - (ii)  $\beta$ -(2-methoxy-5-methylphenyl)-glutaconic acid,
  - (iii)  $\beta$ -(2-methoxy-4-methylphenyl)-glutaconic acid, and
  - (iv)  $\beta$ -(4-methoxy-2-methyl-5-isopropylphenyl)-glutaconic acid
- are detailed in the experimental and the table below.

In the above set of compounds it is now necessary to decide which forms the "cis" and which, the "trans" configuration. The  $\beta$ -arylglutaconic acids employed readily give their anhydrides and they therefore possess the *cis* configuration which may be expected to continue in their esters obtained by Fisher-Spier method. If these esters are condensed with salicylaldehyde in the presence of NaOH or NaOEt under mild conditions of experiment, only one set of products results. These are expected to possess the *cis* form and are shown as such in the experimental, the other set being called the *trans*.

If piperidine is used for this condensation, as mentioned above, both the *cis* and *trans* forms appear.

Further reasons for assigning *cis* and *trans* configuration to particular compounds will be given in a future communication.

It has also been found that if piperidine is used for the condensation of ethyl  $\beta$ -(4-methoxyphenyl)-glutaconate and benzaldehyde then only one form, viz., the *cis* form of the ester is obtained, as is clear from the fact that on hydrolysis of the condensation product, a quantitative yield of the *cis*- $\alpha$ -benzal- $\beta$ -(4-methoxyphenyl)-glutaconic acid, described by Limaye and Bhawe (*loc. cit.*) which readily gives its anhydride, is obtained. This shows that although the condensing agent, piperidine, is necessary for the appearance of *cis* and *trans* forms, in addition to this, it is necessary to have a group like OH present in the molecule of aldehyde which reacts with one of the COOH groups of the glutaconic acid so as to lock it as by coumarin formation in the present case. Further work in this direction is in progress.

#### EXPERIMENTAL

*Expt. No. 1: Ethyl Ester of the trans- $\beta$ -Coumaryl-3- $\beta$ -(4-methoxyphenyl)-acrylic Acid.*—The ethyl  $\beta$ -(4-methoxyphenyl)-glutaconate (2.92 g.) (Limaye and Bhawe, *loc. cit.*) was mixed with salicylaldehyde (2 c.c.), and piperidine (0.5 c.c.) and absolute alcohol (5-7 c.c.) added. The solution was boiled under reflux for 10 hours. The solution, which assumed a deep orange colour, was allowed to cool and stand for 3 to 4 hours, when a crop of lemon-yellow crystals was obtained, m.p.  $158-60^{\circ}$  (without



decomp.). (The mother-liquor was treated as described below in Expt. No. 4). On crystallisation from ethyl alcohol, shining prismatic crystals of the ethyl ester of the *trans*- $\beta$ -coumaryl-3- $\beta$ -(4-methoxyphenyl)-acrylic acid were obtained, m. p. 165° (without decomp.). The ester is insoluble in water; sparingly soluble in benzene, ethyl acetate, alcohol, chloroform and acetic acid, from which it can be crystallised; yield 0.3 g. (Found: C, 71.75; H, 5.33.  $C_{21}H_{18}O_6$  requires C, 72.0; H, 5.14 per cent).

*Expt. No. 2: Methyl Ester of the trans- $\beta$  Coumaryl-3- $\beta$ -(4-methoxyphenyl)-acrylic Acid.*—This was prepared by using the methyl  $\beta$ -(4-methoxyphenyl)-glutaconate (2.64 g.) in the method described above. The methyl ester of the *trans*- $\beta$ -coumaryl-3- $\beta$ -(4-methoxyphenyl)-acrylic acid separated as a crop of yellowish prismatic crystals, m.p. 163° (without decomp.) after crystallisation from methyl or ethyl alcohol. The mother-liquor remaining after the above crop was removed, was further treated as in the Expt. No. 4. The above ester is insoluble in water; sparingly soluble in benzene, ethyl acetate, alcohol, chloroform and acetic acid. (Found: C, 71.18; H, 4.93.  $C_{20}H_{18}O_6$  requires C, 71.4; H, 4.76 per cent).

*Expt. No. 3: trans- $\beta$ -Coumaryl-3- $\beta$ -(4-methoxyphenyl)-acrylic Acid.*—Any of the esters (1 g.), described above, was dissolved in 1N-alcoholic NaOH (20 c.c.) and the solution was boiled under reflux for 10 hours. A little water was added and the alcohol evaporated off on a water-bath; the solution was diluted with water, filtered and acidified with dilute HCl. The *trans*- $\beta$ -coumaryl-3- $\beta$ -(4-methoxyphenyl)-acrylic acid was precipitated as a lemon-yellow solid which was purified by crystallisation from glacial acetic acid or alcohol in light yellow prismatic crystals. The acid is insoluble in water; sparingly soluble in benzene, ethyl acetate, chloroform and ethyl and methyl alcohols, as also acetic acid from which it can be crystallised. After purification it melted at 213° (without decomp.). If 1 g. of the acid of m.p. 213° was dissolved in 10 c.c. of concentrated sulphuric acid and the solution poured in water after a minute, the acid was quantitatively converted into the *cis* acid of m.p. 198°, described in Expt. No. 4. Its mixed melting point with the *cis*-acid of m.p. 198° (Expt. No. 4) showed a marked depression. The acid of m.p. 213° gave no coloration with ferric chloride. (Found: Equiv., 322.5; C, 70.36; H, 4.69. Monobasic acid  $C_{19}H_{16}O_5$  requires equiv., 322; C, 70.80; H, 4.35 per cent).

TABLE I

No.	Substance.		M. p	% Carbon.		% Hydrogen.		Equiv.	
	Name.	Formula.		Found.	Calc.	Found	Calc.	Found.	Calc.
1	<i>trans</i> - $\beta$ -Coumaryl-3- $\beta$ -(4-methoxyphenyl)-acrylic acid	$C_{19}H_{14}O_6$	213°	70.36	70.80	4.69	4.35	322.5	322.0
2	Ethyl ester of (1)	$C_{21}H_{18}O_6$	165°	71.75	72.00	5.33	5.14	—	—
3	Methyl ester of (1)	$C_{20}H_{16}O_6$	163°	71.18	71.13	4.93	4.76	—	—
4	<i>cis</i> Form of (1)	$C_{19}H_{14}O_5$	198° (decomp.)	70.93	70.80	4.83	4.35	322.5	322.0
5	Ethyl ester of (4)		127°	—	—	—	—	—	—
6	Methyl ester of (4)		147°	—	—	—	—	—	—

TABLE I (contd.)

Name.	Formula.	M. p.	% Carbon.		% Hydrogen.		Equiv.	
			Found.	Calc.	Found.	Calc.	Found	Calc.
7 <i>trans</i> - $\beta$ -Coumaryl-3- $\beta$ -(4-methoxy-3-methylphenyl)-acrylic acid.	$C_{20}H_{16}O_5$	212°	71.04	71.43	4.86	4.76	333.5	336.0
8 Ethyl ester of (7)	$C_{22}H_{20}O_5$	152°	72.13	72.52	5.69	5.49	—	—
9 Methyl ester of (7)		168°	—	—	—	—	—	—
10 <i>cis</i> Form of (7)	$C_{20}H_{16}O_5$	240° (decomp.)	70.96	71.43	4.96	4.76	333.3	336.0
11 Ethyl ester of (10)		150°	—	—	—	—	—	—
12 Methyl ester of (10)		153°	—	—	—	—	—	—
13 <i>trans</i> - $\beta$ -Coumaryl-3- $\beta$ -(2-methoxy-5-methylphenyl)-acrylic acid.	$C_{20}H_{16}O_5$	200°	70.91	71.43	4.9	4.76	333.3	336.0
14 Ethyl ester of (13)	$C_{22}H_{20}O_5$	120°	72.19	72.52	5.72	5.49	—	—
15 Methyl ester of (13)		147°	—	—	—	—	—	—
16 <i>cis</i> Form of (13)	$C_{20}H_{16}O_5$	233° (decomp.)	71.12	71.43	4.88	4.76	333.3	336.0
17 Methyl ester of (16)		153°	—	—	—	—	—	—
18 Ethyl ester of (16)		145°	—	—	—	—	—	—
19 <i>trans</i> - $\beta$ -Coumaryl-3- $\beta$ -(2-methoxy-4-methylphenyl)-acrylic acid.	$C_{20}H_{16}O_5$	220°	70.74	71.43	4.87	4.76	333.3	336.0
20 Ethyl ester of (19)	$C_{22}H_{20}O_5$	140°	72.30	72.52	5.63	5.49	—	—
21 Methyl ester of (19)		165°	—	—	—	—	—	—
22 <i>cis</i> Form of (19)	$C_{20}H_{16}O_5$	228° (decomp.)	—	—	—	—	327.8	336.0
23 Methyl ester of (22)		110°	—	—	—	—	—	—
24 <i>trans</i> - $\beta$ -Coumaryl-3- $\beta$ -(4-methoxy-2-methyl-5-isopropylphenyl)-acrylic acid.	$C_{23}H_{22}O_5$	172°	72.9	73.10	5.90	5.82	377.3	378.0
25 Ethyl ester of (24)	$C_{25}H_{26}O_5$	125°	73.36	73.89	6.56	6.40	—	—
26 Methyl ester of (24)		147°	—	—	—	—	—	—
27 <i>cis</i> Form of (24)	$C_{23}H_{22}O_5$	190° (decomp.)	73.12	73.01	5.93	5.82	377.3	378.0
28 Methyl ester of (27)	—	158°	—	—	—	—	—	—
29 Ethyl ester of (27)	—	138°	—	—	—	—	—	—

Expt. No. 4: *cis*- $\beta$ -Coumaryl-3- $\beta$ -(4-methylphenyl)-acrylic Acid.—The mother-liquor, referred to in Expts. 1 and 2 above, was transferred to a flask containing

about 100 c.c. of water and was subjected to steam distillation for about 45 minutes, during which most of the unreacted salicylaldehyde passed over in the distillate. The flask was disconnected and its dark brown semi-solid contents and the supernatant solution were allowed to cool. The supernatant liquid was decanted and filtered and the filtrate was acidified with dilute HCl, when a flocculent white precipitate was first obtained. This soon turned into a grey, friable mass, m.p.  $180^{\circ}$ - $190^{\circ}$ . This was purified by crystallisation from ethyl alcohol or acetic acid, when white needle-like crystals of the *cis*- $\beta$ -coumaryl-3- $\beta$ -(4-methoxyphenyl)-acrylic acid were obtained, m.p.  $198^{\circ}$  (decomp.). Its mixed melting point with the *trans*-acid of m.p.  $213^{\circ}$  showed a marked depression. The acid of m.p.  $198^{\circ}$  is insoluble in water, sparingly soluble in benzene, ethyl acetate, chloroform, ethyl and methyl alcohols and acetic acid from which it could be crystallised. It was found identical with the acid of the same m.p. obtained by the action of sulphuric acid on the *trans*-acid. It gave no coloration with ferric chloride. By the usual Fischer Spier method this acid gave (a) ethyl ester, m.p.  $127^{\circ}$  (without decomp.) and (b) methyl ester, m.p.  $147^{\circ}$  (without decomp.) from each of which the acid could be regenerated by hydrolysis. (Found: Equiv., 322.5; C, 70.93; H, 4.83. Monobasic acid  $C_{18}H_{14}O_6$  requires equiv., 322.0; C, 70.80; H, 4.35 per cent).

By following a similar procedure (as described in Expt. No. 1 to Expt. No. 3) the esters of the  $\beta$ -arylglutaconic acids were condensed with salicylaldehyde in the presence of piperidine and the various products obtained are listed in Table I.

The above work was carried out in author's laboratory at Dadar, Bombay.

BHAVE HOUSE, 105,  
HINDU COLONY,  
DADAR, BOMBAY 14.

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## RELATION BETWEEN VISCOSITY AND GELATION OF AN IRON SILICATE SOL

By G. K. SHUKLA AND S. GHOSH

A sol of iron silicate has been prepared by the interaction of ferric chloride and sodium silicate solutions. The rate of flow of this sol at various stages of purity attained by dialysis has been measured at different pressures causing the flow and also with progressive dialysis. With dialysis the iron content has been found to decrease, but silica content remains practically constant, whilst the impurity as chloride attains a value beyond which further dialysis causes the gelation of the sol within the parchment bag.

The sol has a tendency to yield gels simply by prolonged dialysis, coagulation with suitable amounts of electrolytes, or by simply warming at a certain stage of purity. The results are significant for the measurements of the rate of flow through capillary where it is definitely shown that when the sol begins to deviate from the Poiseuille's law for fluids, either for its concentration or purity, it yields gels. Hence, the tendency of the development of the structural flow is concluded to be intimately related with the capacity for the formation of a gel from a sol.

Some colloids become more viscous when made pure by dialysis and some of these sols show an increase in viscosity, and finally they set to a firm gel on prolonged dialysis, or by coagulation with suitable electrolytes (cf. Banerji and Ghosh, *Proc. Nat. Acad. Sci.*, 1939, 9, 148). In several publications from this laboratory (Ghosh and co-workers, *Kolloid Z.*, 1933, 66, 37; *Proc. Nat. Acad. Sci.*, 1939, 9, 140) it has been pointed out that such sols do not obey Poiseuille's law, for the viscosity of these sols remarkably decreases with increasing shearing force. Ghosh *et al.* ascribe this to the formation of loose structure, and have termed the flow of such sols through a capillary, structural flow, which is similar to plastic flow described by Bingham ("Fluidity and Plasticity", New York, 1922). In this paper the relation of viscosity, specially from the point of view of applicability of Poiseuille's law, with the tendency of gel formation has been studied for an iron silicate sol for various stages of purity attained by dialysis, and it has been established that formation of a gel from a sol of iron silicate is possible only when the sol has developed sufficient structural flow.

### EXPERIMENTAL

Ferric chloride solution (100 c.c.) having 4.3 g. atoms of chlorine per litre, diluted to 400 c.c. with distilled water, was taken to prepare the colloid. Sodium silicate solution (193.9 c.c.) having 11.092 moles of  $\text{Na}_2\text{O}$  and 12.4 moles of  $\text{SiO}_2$  per litre was taken which had  $\text{Na}_2\text{O}$  content equivalent to the total chloride content of the 100 c.c. of the ferric chloride solution and diluted to 1550 c.c. with distilled water. This diluted sodium silicate solution was gradually added to ferric chloride solution with constant stirring. The precipitate of iron silicate formed was peptised by ferric or hydrogen ions and a yellowish red sol of iron silicate resulted. After adding 1200 c.c. of sodium silicate solution the precipitate formed refused to be peptised and a slight precipitation was visible. Hence, the sol was prepared by using lesser amount of sodium

silicate solution than the equivalent quantity. Attempts to prepare the sol containing equivalent quantity failed, as the addition of the equivalent quantity gave precipitates of iron silicate. The sol, thus prepared, contained an excess of ferric chloride and was positively charged. It was filtered through glass wool and kept for dialysis. Samples of different purities were collected and diluted twice, four times and eight times with distilled water so as to give four different concentrations of the sol. The rate of flow relative to that of water for each sample was noted at four different pressures, namely 15 cm., 30 cm., 45 cm., and 60 cm. of the water column by a modified Ostwald's viscometer, first described by Ghosh and Ayub (*Proc. Nat. Acad. Sci.*, 1939, 9, 149), outline diagram of which is given in Fig. 1.

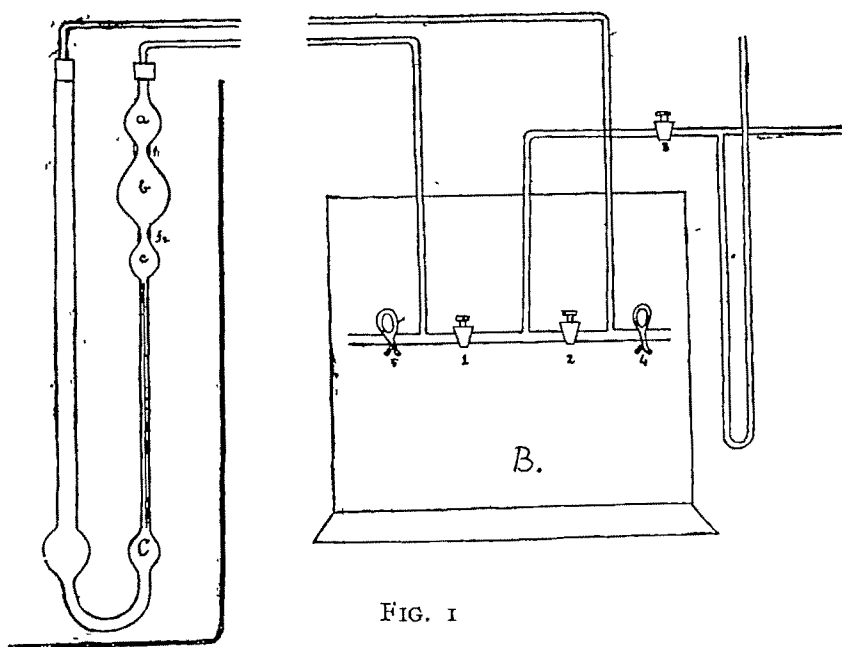


FIG. 1

It consists of an Ostwald's viscometer with three additional bulbs  $a$ ,  $c_1$ ,  $c_2$  of small capacity each besides the main bulb,  $b$ , of the viscometer. These additional bulbs are to store the liquid on the both sides of the capillary and to provide sufficient time for getting the pressure applied uniformly. Three or more Winchester bottles, each about three litres capacity, are wrapped in saw dust for shielding them from the external temperature variations. The air inside them is compressed by connecting them with a large flask in which tap water flows in and creates compression. The Winchester bottles containing compressed air, acting as a source of applying pressure, are connected with a water manometer on one side and to the limb of the viscometer through a board  $B$  of stop-cocks, which provides a device for reversing the pressure in the limb of the viscometer. When the stop-cocks 2 and 5 are closed and 1 and 4 are open, the liquid flows in  $f_1f_2$  direction, i.e., the liquid flows down, while reversing the stop-cock arrangement, i.e., opening 2 and 5 and closing 1 and 4, the liquid flows in the reverse direction, i.e.,  $f_2f_1$  and fills the bulb. The time taken by the liquid to go from  $f_1f_2$  ( $t_1$ )

and then from  $f_2 f_1$  marks ( $t_2$ ) are noted separately. The viscometer is kept in a thermostat. The volume of the liquid is so chosen for the viscometer that the values of  $t_1$  and  $t_2$  do not differ much, so that the average pressure due to the difference in the levels of the liquid in the two limbs of the viscometer is very nearly the same, and the pressure recorded on the manometer is mainly responsible for causing the flow. Measurements are made only up to such a pressure where the turbulent flow of the liquid just appears. In our case, the flow becomes turbulent if the time of flow of the volume of liquid between  $f_1 f_2$  marks becomes less than 1 minute and 15 seconds as determined by the measurement of viscosities of standard fluids. The appropriate volume for our viscometer is 30.5 c.c. The relative viscosity of sols with respect to water is calculated by

$$\eta_s / \eta_w = \frac{1/t_{1w} + 1/t_{2w}}{1/t_{1s} + 1/t_{2s}}$$

where  $\eta_s$  is the viscosity of the sol at a definite temperature and pressure,  $\eta_w$  is the viscosity of water under the same conditions;  $t_{1w}$  and  $t_{2w}$  are the times of flow downwards and upwards respectively for water;  $t_{1s}$  and  $t_{2s}$  denote times of flow downwards and upwards respectively for the sol (cf. Jha and Ghosh, this *Journal*, 1945, 22, 23).

The experimental results described here deal with four samples of iron silicate sols—before dialysis, after 48 hours of dialysis, 96 hours of dialysis, and 144 hours of dialysis, that is, just before seven days, five days, three days, and a day before the sol sets to a gel simply by progressive dialysis. The relative viscosities of each sample and its dilutions were measured at three different temperatures and four different pressures. Each sample was analysed for its iron, silica, and chloride contents.

TABLE I

Sol I.—Sample before dialysis.

Composition:  $\text{Fe}_2\text{O}_3$ , 0.03332 g. mole/litre.

$\text{SiO}_2$ , 0.09524 „ „ „

Cl, 0.19770 g. atom/ „

Iron silicate therefore contains  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  in the ratio of 1.2.89. This sample shows coagulation with electrolytes after boiling. The coagulation gives opaque precipitates.

Pressure in water column. (P).	Temp = 20°				Temp = 40°			
	Sol I. ( $\eta_s/\eta_w$ )	Sol I/2. ( $\eta_s/\eta_w$ )	Sol I/4. ( $\eta_s/\eta_w$ )	Sol I/8. ( $\eta_s/\eta_w$ )	Sol I. ( $\eta_s/\eta_w$ )	Sol I/2. ( $\eta_s/\eta_w$ )	Sol I/4. ( $\eta_s/\eta_w$ )	Sol I/8. ( $\eta_s/\eta_w$ )
15 cms.	1.181	1.101	1.015	1.014	1.180	1.104	1.046	1.027
30	1.179	1.100	1.009	1.007	1.179	1.100	1.043	1.015
45	1.172	1.086	1.009	1.007	1.157	1.096	1.036	1.014
60	1.169	1.079	1.003	1.003	1.147	1.086	1.035	1.014

Pressure in water column.	Temp. = 60°.				Temp. cooled to 60° from 20°.			
	Sol I. ( $\eta_s/\eta_w$ )	Sol I/2. ( $\eta_s/\eta_w$ )	Sol I/4. ( $\eta_s/\eta_w$ )	Sol I/8. ( $\eta_s/\eta_w$ )	Sol I. ( $\eta_s/\eta_w$ )	Sol I/2. ( $\eta_s/\eta_w$ )	Sol I/4. ( $\eta_s/\eta_w$ )	Sol I/8. ( $\eta_s/\eta_w$ )
15 cms.	1.414	1.029	1.074	1.035	1.375	1.162	1.016	1.016
30	1.410	1.126	1.074	1.033	1.356	1.153	1.013	1.009
45	1.392	1.106	1.058	1.030	1.352	1.153	1.010	1.007
60	1.374	1.076	1.001	1.018	1.330	1.144	1.066	1.006

TABLE II

Sol II.—Sample taken after 48 hours of dialysis.

*Composition* :  $\text{Fe}_2\text{O}_3$ , 0.0312 g. mole/litre.

$\text{SiO}_2$ , 0.0953 ,, ,, ,,

Cl, 0.03029, atom/ ,,

It contains  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  in the ratio of 1:3.05. The sample shows coagulation by electrolytes on warming and the precipitates become opaque red.

Pressure in water column.	Temp. = 20°.				Temp. = 40°.			
	Sol II. ( $\eta_s/\eta_w$ )	Sol II/2. ( $\eta_s/\eta_w$ )	Sol II/4. ( $\eta_s/\eta_w$ )	Sol II/8. ( $\eta_s/\eta_w$ )	Sol II. ( $\eta_s/\eta_w$ )	II/2. ( $\eta_s/\eta_w$ )	II/4. ( $\eta_s/\eta_w$ )	II/8. ( $\eta_s/\eta_w$ )
15 cms.	1.300	1.035	1.014	1.010	1.262	1.140	1.038	1.030
30	1.254	1.030	1.007	1.009	1.254	1.140	1.029	1.022
45	1.240	1.021	1.006	1.000	1.254	1.139	1.027	1.019
60	1.237	1.012	1.003	1.000	1.252	1.138	1.024	1.012

	Temp. = 60°.				Temp. cooled from 60° to 20°			
	II.	II/2.	II/4.	II/8.	II.	II/2.	II/4.	II/8.
15 cms.	1.413	1.148	1.084	1.034	1.483	1.114	1.023	1.018
30	1.396	1.131	1.078	1.033	1.469	1.110	1.022	1.012
45	1.396	1.112	1.078	1.031	1.469	1.102	1.020	1.010
60	1.394	1.109	1.066	1.019	1.450	1.102	1.012	1.006

TABLE III

Sol III.—Sample taken after 96 hours of dialysis.

*Composition* :  $\text{Fe}_2\text{O}_3$ , 0.030 g. mole/litre.

$\text{SiO}_2$ , 0.09526 ,, ,,

Cl, 0.0083 ,, atom/ ,,

Iron silicate therefore contains  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  in the ratio of 1:3.08. The sol yields gelatinous precipitates on coagulation with electrolytes.

Pressure in water column.	Temp. = 20°.				Temp. = 40°.			
	III. ( $\eta_s/\eta_w$ )	III/2. ( $\eta_s/\eta_w$ )	III/4. ( $\eta_s/\eta_w$ )	III/8. ( $\eta_s/\eta_w$ )	III. ( $\eta_s/\eta_w$ )	III/2. ( $\eta_s/\eta_w$ )	III/4. ( $\eta_s/\eta_w$ )	III/8. ( $\eta_s/\eta_w$ )
15 cms.	1.325	1.052	1.018	1.018	1.315	1.152	1.040	1.028
30	1.312	1.046	1.017	1.017	1.320	1.148	1.035	1.028
45	1.286	1.035	1.012	1.016	1.309	1.143	1.034	1.020
60	1.280	1.032	1.007	1.006	1.286	1.136	1.030	1.017

	Temp. = 60°.				Temp. cooled from 60° to 20°.			
	III.	III/2.	III/4.	III/8.	III.	III/2.	III/4.	III/8.
15 cms.	1.394	1.147	1.042	1.028	1.493	1.086	1.048	1.031
30	1.380	1.152	1.038	1.028	1.462	1.057	1.045	1.029
45	1.366	1.148	1.035	1.022	1.452	1.052	1.040	1.029
60	1.348	1.140	1.034	1.020	1.425	1.052	1.036	1.022

TABLE IV

Sol. IV.—Sample taken after 144 hours of dialysis.

Composition:  $\text{Fe}_2\text{O}_3$ , 0.02907 g. moles/litre.

$\text{SiO}_2$ , 0.09524 „ „

Cl, 0.0083 „ atom/ „

Iron silicate therefore contains  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  in the ratio of 1:3.27. The sol yields good gels which are transparent, on coagulation with electrolytes, or by heating up to 65° within 5 to 10 minutes.

Pressure in water column.	Temp. = 20°.				Temp. = 40°.			
	Sol IV ( $\eta_s/\eta_w$ )	Sol IV/2. ( $\eta_s/\eta_w$ )	Sol IV/4. ( $\eta_s/\eta_w$ )	Sol IV/8. ( $\eta_s/\eta_w$ )	Sol IV ( $\eta_s/\eta_w$ )	Sol IV/2. ( $\eta_s/\eta_w$ )	Sol IV/4. ( $\eta_s/\eta_w$ )	Sol IV/8. ( $\eta_s/\eta_w$ )
15 cms.	2.767	1.264	1.028	1.029	2.843	1.287	1.098	1.043
30	2.639	1.254	1.023	1.023	2.665	1.274	1.096	1.046
45	2.585	1.242	1.022	1.022	2.525	1.266	1.093	1.040
60	2.521	1.223	1.002	1.016	2.393	1.266	1.093	..

	Temp. = 60°.				Temp. cooled from 60° to 20°.			
	Sol IV.	Sol IV/2.	Sol IV/4.	Sol IV/8.	IV.	IV/2.	IV/4.	IV/8.
15 cms.	No flow	3.216	1.263	Complete pptn. but no gela- tion.	The whole vol. set to a firm gel.	32.280	1.410	—
30	..	2.507	1.241	..	„	2.856	1.335	—
45	..	1.997	1.248	..	„	2.616	1.293	—
60	87.44	1.697	1.248	..	„	2.423	1.266	—



The sol IV being sufficiently pure shows large variations of  $\eta_s/\eta_w$  with changes in the pressure causing flow. Hence, this sol with remarkable structural flow can easily be coagulated with electrolytes and is seen to yield gels at room temperature. The cataphoretic coagulation under suitable condition also yields gels. The water associated with a certain volume of sol in gelation, that is, the dilution up to which this sol shows gelation after coagulation with a fixed concentration of ammonium sulphate, is shown in the following table.

TABLE V

N/100. Ammonium sulphate = 0.7 c.c. Water added = 0.3 c.c. Total vol. of the electrolyte (used in each case) = 1.0 c.c.

Volume of sol IV.	Vol. of water added	Nature of precipitate.
2.0 c.c.	0.0 c.c.	Red, transparent gel without syneresis.
1.8	0.2	Do
1.6	0.4	Do
1.4	0.6	Do; syneresis pronounced.
1.3	0.7	Gelatinous ppt.

The results obtained on analysis of different samples of the sol show that the amount of iron goes on continuously decreasing with progressive dialysis. The amount of silica remains practically constant throughout the dialysis. The amount of chloride ion decreases quickly and finally reaches a constant value, which cannot be removed by further dialysis. Ferric chloride at earlier stages passes out which is in excess. Finally  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  ratio becomes 1 : 3.27. Further dialysis leads to the formation of the sol as a transparent gel.

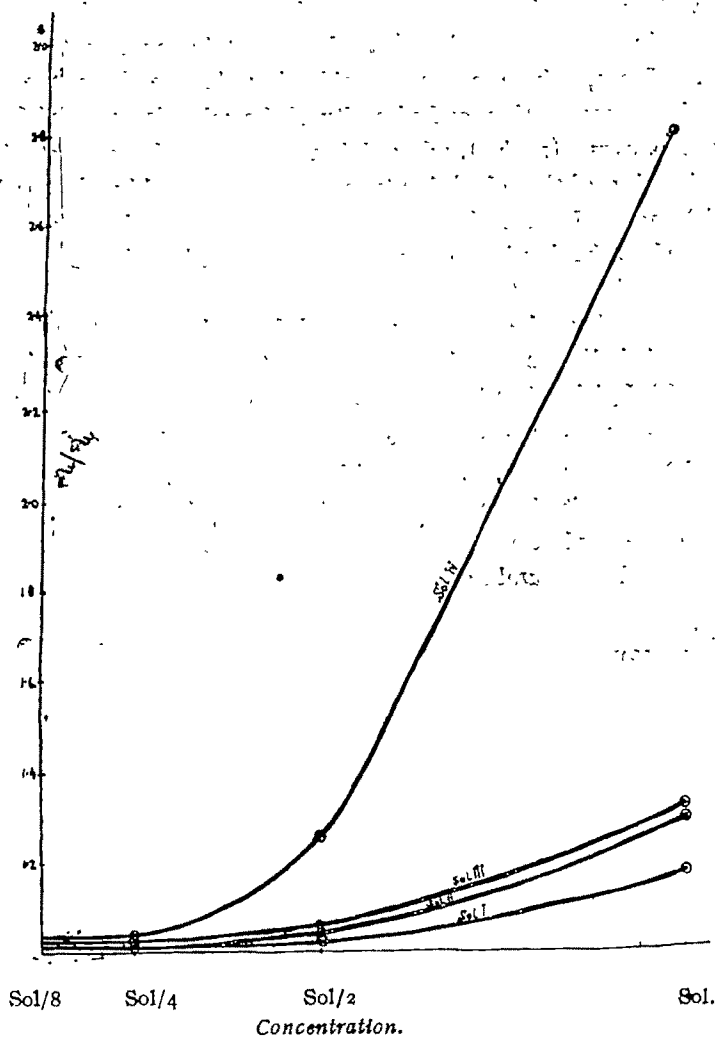
Iron silicate shows the evidence of the variation in the value of  $\eta_s/\eta_w$  at different pressures effecting the flow from the very beginning (cf. Dissert., Heidelberg; *Phil. Mag.*, 1903, 6, 374). These variations become more and more pronounced as the purity of the sol increases. For example, at 20°, sol I shows a change of 1.020% in the rate of flow for the variation of the pressure from 15 cm. to 60 cm. of water column. This change in the rate of flow increases to 9.7% for the variation in pressure causing flow, from 15 cm. to 60 cm. of water column in case of sol IV which is much pure for practically the same concentration of the sol. By prolonged dialysis the viscosity as well as the structural flow of the sol increases (cf. Bingham and Green, *Proc. Amer. Soc. Test. Mat.*, 1919, 19, 641) and when the structural flow becomes very prominent at a certain stage of purity, the gelation can be effected by the addition of electrolytes.

The coagulation of the sol is helped as the temperature is increased. In all cases this is seen to be true and the gelation is facilitated in cases of purer sols. In samples I, II, III, it can be seen that the amount of structural flow increases with the increase of temperature (cf. *Proc. Nat. Acad. Sci.*, 1939, 9, 148, 153); in the case of sol IV it increases very remarkably. Similar results have been reported by Banerji and Ghosh (*loc. cit.*) for ferric phosphate sol. At 60° sol IV sets to a gel without the addition of any electrolyte which also develops an enormous increase in the structural flow and in the so-called viscosity at that temperature.

When these sols are cooled again to  $20^{\circ}$ , there is a definite increase in the values of  $\eta_s/\eta_w$  and the increase in the structural flow can be noted by comparing the data of the sol at that temperature before heating. Coagulation and gelation, thus, are favoured by heating.

In sols which set to a gel condition by progressive dialysis, as this particular one is, it is customary to ascribe it to the increased hydration by dialysis (Prakash and Dhar, this *Journal*, 1929, 6, 391; 1930, 7, 417). After a stage of purity, the hydration of the colloid particle sets the sol to a firm gel, retaining a large volume of liquid (Satya Prakash, *J. Soc. Chem. Ind.*, 1931, 50, 387T). If it is so, the gel formation may not be facilitated by the increase of temperature, as by heating it the hydration decreases, while it is clear from our results that the structural flow becomes more pronounced with the increase of temperature. Hence, the structure and not the hydration should be related with the phenomenon of gelation.

FIG. 2



As the sol is diluted, its structural flow and necessarily  $\eta_s/\eta_w$  are seen to decrease but up to twice its dilution the decrease is not so great as it occurs in diluting the sol to 4 or 8 times. Our results show that the tendency of gelation is also seen to decrease by the addition of electrolytes. In the sol IV it is seen that the structural flow is prominent for the sol IV/2, and for sol IV/4 it becomes practically insignificant. The results show that the sol IV, when diluted twice, gives a gel, but when diluted four times only gelatinous precipitates are seen after coagulation, which shows undoubtedly that the structural flow and the tendency of gelation are seen to decrease with dilution.

It can be concluded that the colloid of iron silicate under investigation has got the structural flow from the very beginning which increases with purity. After a certain stage of purity the sol can be transformed to a gel by simple heating, by cataphoresis, by progressive dialysis, or by adding electrolytes under suitable conditions.

In Fig. 2 changes in the values of  $\eta_s/\eta_w$  against the concentration of the sols are plotted. One fact will be seen clearly from the curves that as the sols become purer and begin yielding gelatinous precipitates with increasing purity, there is always a sudden increase in the values of  $\eta_s/\eta_w$  after a certain concentration say, when it is diluted 4 times. Hence, these curves considerably deviate from the simple linear relationship of the concentration and viscosity of the sol as is expected from the simple equation of Einstein,  $\eta_s = \eta_w(1 + k\phi)$ , where  $k$  is a constant and represents the concentration, and the viscosity of the sol of this type is common to all lyophilic sols which have a tendency to yield gels. In several communications from this laboratory, this behaviour has been associated to the development of a structure and it will be seen from the curves that for the sol IV the increment in the values of  $\eta_s/\eta_w$  becomes remarkable, increasing from 1.028 to 2.767 when the concentration of the sol becomes 8 times with respect to the former one. This indicates a tendency of the sol to form gels, and as has been already pointed out, the sol IV yields firm transparent gels only up to twice its dilution.

In the sol-gel transformation, not only the hydration of the colloid particles but a development of loose structure, as recorded by the values of  $\eta_s/\eta_w$  at variable pressure, is of great importance and it shows a direct relation to the gelation tendency of the sol. Even where the hydration is not likely to increase, the sol yields a good gel if the sol shows a pronounced structural flow.

# STUDIES ON 'LIPASE' FROM OIL SEEDS. PART VI. HYDROLYSIS OF SOME ALIPHATIC ESTERS BY RICINUS LIPASE

By C. V. RAMAKRISHNAN AND G. V. NEVGI

Hydrolysis of some esters of butyric and propionic acids was carried out using acetone-dried lipase in order to study the effect of change of the number of carbon atoms in the alcohol on the hydrolysis of esters by lipase.

The hydrolysis of some aliphatic esters was carried out using acetone-dried lipase in order to study the effect of the number of carbon atoms in the alcohol and acid on the hydrolysis of esters. So the hydrolysis of methyl, ethyl, *n*- and isopropyl, *n*- and isobutyl, *n*- amyl esters of propionic and butyric acids was carried out.

## EXPERIMENTAL

In each flask 0.018 g. mol. of ester solution, 1 g. of lipase and 10 c.c. of ether solvent and a few drops of toluene were taken and incubated at 37°. At different intervals of time, 1 c.c. portion of it was taken, neutral alcohol (25 c.c.) added, warmed for some time and titrated against *N*/10 sodium hydroxide. The initial reading was also taken before starting the experiment. From the difference in readings, the percentage hydrolysis was calculated. The results are shown in Table I.

TABLE I

Esters.	Percentage hydrolysis on days.					
	1 st	2 nd.	3 rd.	4 th.	5 th.	6 th.
Methyl propionate	40.1	44.8	49.2	50.8	48.5	—
Ethyl „	45.0	48.5	50.7	51.9	51.5	—
<i>n</i> -Propyl „	37.0	39.2	42.5	46.7	45.8	—
<i>iso</i> Propyl „	17.2	19.1	24.8	31.6	35.8	34.5
<i>n</i> -Butyl „	20.4	24.7	31.2	34.5	33.6	—
<i>iso</i> Butyl „	21.6	25.0	32.6	33.9	32.5	—
<i>n</i> -Amyl „	14.9	25.8	33.7	32.5	—	—
Methyl butyrate	44.0	46.0	51.5	50.5	—	—
Ethyl „	45.5	51.5	43.5	—	—	—
<i>n</i> -Propyl „	38.2	40.9	43.7	45.9	43.7	—
<i>iso</i> Propyl „	15.5	18.8	22.6	39.2	36.7	34.8
<i>n</i> -Butyl „	21.2	23.8	30.9	33.7	32.3	—
<i>iso</i> Butyl „	22.6	25.8	33.4	33.7	31.8	—
<i>n</i> -Amyl „	19.8	28.1	29.2	31.2	30.5	—

From the above table, it is found that the percentage hydrolysis goes on decreasing from methyl to amyl butyrate and methyl to amyl propionate, and so it can be inferred that the increase in the number of carbon atoms in the alcohol decreases the percentage hydrolysis from methyl to amyl ester. In other words, the hydrolysis is difficult in case of higher esters.

The percentage hydrolysis is always greater in case of the *normal* ester than the *iso* one. In the case of *n*- and isopropyl esters, the difference in percentage hydrolysis may be due to difference in structure [*n*-propyl ester is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOC}_3\text{H}_7$  and isopropyl ester is  $(\text{CH}_3)_2\text{CH}\cdot\text{COOC}_3\text{H}_7$ ], whereas in the case of *n*- and isobutyl esters, the difference in percentage may be due to the difference in densities (density of *n*-butyl ester is 0.872 and the density of isobutyl ester is 0.861) as their structures are the same.

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# STUDIES ON 'LIPASE' FROM OIL SEEDS: PART VII. HYDROLYSIS OF SOME ALIPHATIC ESTERS

BY C. V. RAMAKRISHNAN AND G. V. NEVGI

Hydrolysis of butyl and amyl formate, acetate, propionate and butyrate has been carried out using acetone-dried lipase in order to study the effect of change of the number of carbon atoms in the acid on the hydrolysis of esters by lipase.

The hydrolysis of butyl and amyl formate, acetate, propionate and butyrate by ricinus lipase was carried out in order to study the effect of change of the number of carbon atoms in the acid on the enzymic hydrolysis of esters. The results are shown in the following table.

TABLE-I

Esters.	Percentage hydrolysis on days					
	1 st.	2 nd.	3 rd.	4 th.	5 th.	6 th.
Butyl formate	20.9	22.9	29.8	34.0	33.2	—
„ acetate	19.8	25.7	32.4	35.3	35.0	—
„ propionate	20.4	24.7	31.2	34.5	33.6	—
„ butyrate	21.2	23.8	30.9	33.7	32.3	—
Amyl formate	10.8	19.2	23.2	28.2	30.9	—
„ acetate	16.1	20.8	31.8	30.4	—	—
„ propionate	14.9	25.8	33.7	32.5	—	—
„ butyrate	19.8	28.1	29.2	31.2	30.5	—

From the above table the maximum percentage hydrolysis is found to be almost the same in case of all the four esters in each group and so it can be inferred that the change of the number of carbon atoms in the acid does not affect the percentage hydrolysis of esters. In other words, the hydrolysis of esters is independent of the number of carbon atoms in the acid and only depends upon the number of carbon atoms in the alcohol.

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## STUDIES ON 'LIPASE' FROM OIL SEEDS. PART VIII. EFFECT OF SALTS ON THE SYNTHESIS AND HYDROLYSIS OF SOME ESTERS BY LIPASE

By C. V. RAMAKRISHNAN AND G. V. NEVGI

The effect of different salts on the synthesis and hydrolysis of some esters by lipase has been studied with a view to obtaining some idea as regards the effect of the nature of the ions on the synthesis and hydrolysis of esters by ricinus lipase.

Rona and Ammon (*Biochem. Z.*, 1931, **241**, 460) studied the action of calcium chloride, quinine chloride and stychnine sulphate on the synthesis and hydrolysis of *n*-butyl *n*-butyrate by pancreatic lipase. Ramakrishnan and Nevgi (M.Sc. thesis, University of Bombay, 1947) have found that the synthesis and hydrolysis of esters can be carried out in ether solvent using lipase from castor seed.

The action of the following substances on the synthesis and hydrolysis of esters was studied in order to find out good accelerators: acetic acid, KCN, NaCl, CaCl<sub>2</sub>, AlCl<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, MgSO<sub>4</sub>, MnSO<sub>4</sub>, BaCl<sub>2</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

### EXPERIMENTAL

*N*/10- solutions of the above substances and the acetone-dried lipase from castor seeds were used for the experiments. Each set of experiments consisted of equimolecular quantities (0.054 g. mol.) of acid and alcohol, 1 g. of lipase, 10 c.c. of ether solvent and 1 c.c. of salt solution. The blank experiment was also carried out side by side. All were kept in the incubator at 37° and at different intervals of time 1 c.c. of each was taken, neutral alcohol (25 c.c.) added, warmed and titrated against *N*/10 sodium hydroxide. The results of the percentage synthesis in the form of difference in c.c. of *N*/10- NaOH between the sample and the blank in case of each salt were calculated. The difference between the two readings shows whether a particular salt is an accelerator or inhibitor depending upon whether the difference is a positive one (showing accelerating effect) or a negative one (showing retarding effect). The results in the form of maximum synthesis reached in each case are given in Table I.

For hydrolysis experiment, each set of the experiments consisted of 0.018 g. mol. of each ester solution, 1 g. of lipase, 10 c.c. of ether solvent and 1 c.c. of salt solution. The blank was carried out side by side. All were kept in the incubator at 37°. At different intervals of time 1 c.c. of each was taken, neutral alcohol (25 c.c.) added and titrated against *N*/10 NaOH. The difference in reading between the sample and the blank shows whether a particular salt is an accelerator or retarder. The results in terms of maximum hydrolysis reached in each case are given in Table II.

From Table I, it can be seen that in general, CaCl<sub>2</sub>, BaCl<sub>2</sub> and MnSO<sub>4</sub> are the best accelerators for most of the synthesis experiments and AlCl<sub>3</sub>, Na<sub>2</sub>HPO<sub>4</sub>, NaCl and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> act as poisons in most of the cases.

TABLE I

*Synthesis experiments.*

Name of the esters.	Maximum synthesis reached in terms of difference in c.c. of N/10-NaOH between the sample and blank for									
	CH <sub>3</sub> CO <sub>2</sub> H	KCN.	NaCl.	CaCl <sub>2</sub>	AlCl <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> HPO <sub>4</sub>	MgSO <sub>4</sub>	MnSO <sub>4</sub>	BaCl <sub>2</sub>
Methyl butyrate	+2.0	4.7	5.0	6.7	-6.6	-31.2	1.5	2.8	4.2	5.2
Ethyl "	1.4	1.3	0.3	2.5	-1.1	2.3	-0.3	2.8	0.7	0.9
n-Propyl "	1.2	3.2	-2.0	1.8	-1.8	0.4	-2.1	4.8	3.1	13.6
iso-Propyl "	6.3	2.8	-1.8	2.8	-0.1	1.2	0.6	0.2	3.2	1.6
n-Butyl "	-1.2	-0.9	-2.7	2.7	2.0	0.4	2.2	-3.8	4.0	4.3
iso-Butyl "	2.3	3.9	-1.3	4.1	2.3	3.8	2.5	1.4	3.8	5.1
n-Amyl "	4.2	3.2	-5.3	5.2	-1.8	0.2	-1.0	1.7	2.8	2.1
iso-Amyl "	-4.1	4.2	2.8	3.8	3.9	3.5	-4.1	-1.7	2.2	8.7
Amyl formate	0.3	1.3	-2.1	1.8	-2.2	-1.9	-4.2	4.1	4.6	5.1
Amyl acetate	-0.5	-2.1	1.3	5.1	-1.5	1.4	2.3	-0.4	4.2	7.2
Amyl propionate	1.2	3.1	0.5	4.6	-1.8	0.4	1.2	2.8	1.6	5.3

TABLE II

	Maximum hydrolysis reached in terms of difference in c.c. of N/10-NaOH between the sample and blank for									
	CH <sub>3</sub> CO <sub>2</sub> H.	KCN.	NaCl.	CaCl <sub>2</sub>	AlCl <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> HPO <sub>4</sub>	MgSO <sub>4</sub>	MnSO <sub>4</sub>	BaCl <sub>2</sub>
Methyl butyrate	3.7	10.2	4.6	5.2	5.6	5.9	3.5	7.0	9.4	7.0
Ethyl "	3.7	1.5	1.3	1.4	1.6	3.7	2.3	3.1	3.9	4.5
n-Propyl "	8.9	10.2	8.2	8.5	7.5	0.0	5.9	7.2	8.7	7.7
iso-Propyl "	5.2	7.2	5.0	7.2	3.1	2.2	6.5	6.1	9.9	4.1
n-Butyl "	-0.7	3.8	2.0	1.8	-0.8	-2.1	-1.7	0.5	1.2	-2.3
iso-Butyl "	1.8	4.5	-1.8	1.2	0.4	-1.8	0.0	3.1	4.1	2.1
n-Amyl "	2.6	10.7	0.6	3.1	1.6	1.8	1.9	2.5	13.0	2.4
iso-Amyl "	4.6	4.9	0.4	3.4	1.0	3.8	2.6	3.5	11.8	1.6
Amyl formate	3.4	1.5	1.8	4.2	0.6	2.6	2.1	2.3	4.6	1.1
Amyl acetate	5.3	2.8	-0.3	1.5	1.4	4.2	2.9	3.8	10.6	2.8
Amyl propionate	-1.1	3.8	1.2	-2.2	1.4	1.9	3.1	-3.2	11.2	4.2



From Table II, it is found that KCN and  $\text{MnSO}_4$  are the best accelerators for hydrolysis of most of the esters.  $\text{K}_2\text{Cr}_2\text{O}_7$  in general has got least accelerating power.

So it can be seen that  $\text{MnSO}_4$  is a good accelerator for synthesis as well as hydrolysis of esters by lipase and  $\text{K}_2\text{Cr}_2\text{O}_7$  in general has got least accelerating power.

In some cases, it is found that one salt, which appears to be the best accelerator in one case, acts as a retarder in other case. Hence, a definite conclusion cannot be arrived at as regards the effect of nature of the salts on the synthesis and hydrolysis of esters by lipase.

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# ARTICLE

## STUDIES ON LIPASE FROM OIL SEEDS. PART IX. COMPARATIVE STUDY OF THE LIPASES FROM DIFFERENT OIL SEEDS

BY C. V. RAMAKRISHNAN AND G. V. NEVGI

A comparative study of the lipases prepared from castor, safflower and sesame seeds has been made.

An attempt has been made to get a sample of lipase which is more active than castor lipase. So the lipase was extracted from sesame (*Sesamum indicum*) and safflower seeds (*Carthamus tinctorius*) and their activities compared with that of castor lipase.

The lipases of castor seed, sesame and safflower were prepared according to Longnecker and Haly's method (*J. Amer. Chem. Soc.*, 1935, 57, 2619) and used for the experiments.

### EXPERIMENTAL

#### *Effect of the Nature of the Buffer and the Nature of the Substrate on the Activity of Lipases from the Three Seeds*

The effect of different buffers on the activity of the lipase and the optimum  $p_H$  in case of each buffer have been studied in different oils like olive-oil, castor oil, sesame oil and safflower oil in order to ascertain the effect of the nature of the buffer as well as the nature of the substrate on the optimum  $p_H$  of the lipase.

The three buffers : disodium phosphate - citric acid, sodium acetate-hydrochloric acid and sodium acetate-acetic acid buffer mixtures of different  $p_H$  were prepared according to McIlvaine and Walpole's methods (*J. Biol. Chem.* 1921, 49, 183) respectively and used for the experiment.

Each set of the experiments consisted of different oil (1 c.c.), water (2 c.c.), different lipases (0.1 g.), different buffer (5 c.c.) of varying  $p_H$  and a few drops of toluene in a conical flask, corked well and incubated for 24 hours at 37°. Always a blank accompanied each sample. After the period of incubation, each flask was taken out and the contents titrated against  $N/10$ -NaOH. The results are given in the following tables.

From the tables below, it is found that in case of castor seed lipase, the optimum  $p_H$  is 4.8 in disodium phosphate-citric acid and sodium acetate-hydrochloric acid buffer and 4.9 in sodium acetate-acetic acid buffer (variation being negligible) irrespective of the nature of the oil used as a substrate. The maximum percentage hydrolysis of the oil by castor seed lipase decreases in the order : castor oil, olive oil, sesame oil and safflower oil. As regards the nature of the buffer, the activity is always more in sodium acetate-acetic acid buffer and less in case of disodium phosphate-citric acid buffer.

In case of sesame lipase, the optimum  $p_H$  is always 5.5. The maximum percentage hydrolysis decreases in the order : sesame oil, olive oil, castor oil and safflower oil.

TABLE I

Buffer : disodium phosphate-citric acid.

Diff. bet the sample and the blank in terms of c. c. of  $N/10$ -NaOH in case of

Set No.	$p_H$ .	Castor lipase.	Seasame lipase.	Safflower lipase.	Castor lipase.	Seasame lipase.	Safflower lipase.
Olive oil (1 c.c.).				Castor oil (1 c.c.).			
1	2.4	3.1	1.9	1.2	4.2	0.9	0.5
2	2.8	4.8	2.2	1.7	5.0	1.2	0.8
3	3.1	4.9	2.6	2.0	7.6	1.8	1.1
4	4.8	5.0	3.0	2.4	8.0	2.5	1.4
5	5.2	0.7	3.1	2.7	3.4	2.7	1.7
6	5.5	0.5	3.8	3.0	2.8	3.1	1.9
7	5.7	1.0	2.9	3.4	2.6	2.6	2.8
8	6.2	0.2	2.2	2.5	2.1	2.1	2.0
Seasame oil (1 c.c.).				Safflower oil (1 c.c.).			
1	2.4	2.1	2.2	0.9	1.5	0.8	0.9
2	2.8	2.6	2.5	1.1	1.7	1.1	1.2
3	3.1	2.9	2.8	1.5	1.9	1.3	1.5
4	4.8	3.8	3.0	1.7	2.1	1.5	1.9
5	5.2	0.3	3.3	2.0	0.2	1.9	2.2
6	5.5	0.2	4.2	2.2	0.2	2.9	2.8
7	5.7	0.2	3.8	3.0	0.1	2.1	3.7
8	6.2	0.1	3.5	2.7	0.1	1.8	3.3

TABLE II

Buffer : sodium acetate-hydrochloric acid.

Diff. bet. the sample and the blank in terms of c. c. of  $N/10$ -NaOH in case of

Set No.	$p_H$ .	Castor lipase.	Seasame lipase.	Safflower lipase.	Castor lipase.	Seasame lipase.	Safflower lipase.
Olive oil (1 c.c.).				Castor oil (1 c.c.).			
1	1.5	0.9	1.1	0.7	1.5	0.5	0.4
2	2.9	7.9	1.5	1.2	8.2	1.1	0.8
3	3.8	13.8	2.3	1.8	15.6	1.6	1.2
4	4.3	15.3	3.4	2.3	18.8	2.2	1.4
5	4.8	19.6	5.2	2.9	22.6	2.9	1.8
6	5.2	2.5	6.1	3.1	10.1	3.2	2.0
7	5.5	2.2	7.1	3.7	7.8	5.8	2.4
8	5.7	1.6	5.7	4.8	5.2	4.0	3.8
9	6.0	1.1	4.2	4.2	2.3	3.5	2.7

TABLE II (contd.)

Diff. bet. the sample and the blank in terms of c.c. of  $N/10$ -NaOH in case of

Set No.	pH	Castor lipase.	Sesame lipase.	Safflower lipase.	Castor lipase.	Sesame lipase.	Safflower lipase.
Sesame oil (1 c.c.).				Safflower oil (1 c.c.).			
1	1.5	2.4	1.2	0.5	1.4	0.5	0.4
2	2.9	3.5	2.5	0.9	2.8	0.8	1.1
3	3.8	7.8	3.8	1.1	5.4	1.2	1.8
4	4.3	11.2	4.1	1.8	9.5	1.9	2.3
5	4.8	15.2	4.9	2.1	12.2	2.8	3.1
6	5.2	10.5	5.3	2.3	10.1	3.1	3.9
7	5.5	9.8	9.8	2.9	8.5	4.5	4.2
8	5.7	7.2	6.5	4.1	8.0	4.3	5.2
9	6.0	5.9	5.2	3.4	7.2	3.9	4.8

TABLE III

Buffer: sodium acetate-acetic acid.

Diff. bet. the sample and the blank in terms of c.c. of  $N/10$ -NaOH in case of

Set No.	pH	Castor lipase.	Sesame lipase.	Safflower lipase.	Castor lipase.	Sesame lipase.	Safflower lipase.
Olive oil (1 c.c.).				Castor oil (1 c.c.).			
1	3.8	7.1	7.2	0.8	6.4	1.2	0.8
2	4.1	11.2	2.4	1.1	12.9	2.3	1.1
3	4.8	15.8	3.6	1.6	21.8	3.8	1.8
4	4.9	31.7	4.8	2.4	38.4	4.1	2.0
5	5.5	10.5	9.2	3.8	25.6	6.5	2.5
6	5.7	7.3	7.5	5.7	20.2	5.2	4.2
7	5.9	5.8	6.2	4.1	18.9	4.3	3.8
8	6.0	4.3	6.0	3.9	17.2	3.9	3.1
Sesame oil (1 c.c.).				Safflower oil (1 c.c.).			
1	3.8	3.8	2.9	0.9	3.2	1.2	1.9
2	4.1	7.9	3.2	1.8	5.7	1.8	2.4
3	4.8	12.5	4.7	2.3	11.5	2.1	3.1
4	4.9	18.3	5.8	3.4	16.8	3.5	3.9
5	5.5	14.3	11.2	3.8	14.3	5.8	5.0
6	5.7	12.1	9.1	4.9	12.8	4.2	6.8
7	5.9	10.1	8.7	4.5	11.6	3.9	4.9
8	6.0	9.7	8.3	4.1	10.9	3.2	3.7

In case of safflower lipase, the optimum  $p_H$  is 5.7. The maximum percentage hydrolysis decreases in the order: safflower oil, olive oil, sesame oil and castor oil. Thus, the optimum  $p_H$  in case of castor, sesame and safflower lipases are 4.8 (or 4.9), 5.5 and 5.7 i.e., each lipase has got its own optimum  $p_H$ . Further, they do not change either with the nature of the oil or with that of the buffer used. The activity is always the least in disodium phosphate-citric acid buffer and more in sodium acetate-acetic acid buffer in all cases. In case of each lipase, there is maximum hydrolysis in its own oil and olive oil in general is a good substrate.

#### *Effect of Buffer Concentration on the Enzymic Hydrolysis of Olive Oil*

The hydrolysis of olive oil was carried out using different concentrations of sodium acetate-acetic buffer of  $p_H$  4.9 and the three kinds of lipases in order to study the effect of change of buffer concentration on the enzymic hydrolysis. The amount of buffer added was varied from 1 to 7 c.c.

Each set of the experiments consisted of olive oil (1 c.c.), water (2 c.c.), different lipases (0.1 g.) and varying quantities of acetate buffer of  $p_H$  4.9 and incubated for 24 hours at 37°. Always the blank was carried out. After the period of incubation, the contents of each flask were titrated against  $N/10$ -NaOH after adding 25 c.c. of neutral alcohol. The results are given in the following table.

TABLE IV

Oil taken = 1 c.c.

Set No.	Buffer added.	Diff. in c.c. of $N/10$ -NaOH between the sample & the blank for		
		Castor lipase.	Sesame lipase.	Safflower lipase.
1	1.0 c.c.	29.1	4.0	3.4
2	2.0	23.2	3.6	3.0
3	3.0	18.4	2.8	2.6
4	4.0	16.0	2.3	2.3
5	5.0	14.9	1.8	2.0
6	6.0	12.3	1.4	1.8
7	7.0	11.0	0.7	1.6

From the results it is found that the percentage hydrolysis is the maximum at the concentration of 1 c.c. and goes on decreasing with the increase of buffer concentration.

#### *Effect of Substrate Concentration on the Hydrolysis of Olive Oil*

The hydrolysis of olive oil was carried out using the three different kinds of lipases by changing the concentration of the oil and keeping the other quantities constant in order to study the effect of the substrate concentration on the enzymic hydrolysis of olive oil.

Each set of the experiments consisted of varying quantities of olive oil, water (2 c.c.), different lipases (0.1 g.) and 1 c.c. of acetate buffer of 4.9 pH, incubated for 24 hours at 37°. After the period of incubation, the contents were titrated against  $N/10$ -NaOH after the addition of 25 c.c. of neutral alcohol and warming for some time. Always each set was accompanied by a blank. The results are given in the following table.

TABLE V

Diff. in c.c. of $N/10$ -NaOH bet. the sample and the blank for				
Set No.	Oil in c.c.	castor lipase	sesame lipase	safflower lipase
1	1.0	41.8	3.4	2.1
2	2.0	49.2	3.9	2.8
3	3.0	56.1	5.2	3.7
4	4.0	53.2	4.9	3.6
5	5.0	47.0	4.7	3.6
6	6.0	41.3	4.0	3.4

In all the three cases the percentage hydrolysis of the oil increases with the substrate concentration from 1 to 3 c.c. and after 3 c.c. it begins to decrease. Therefore, the maximum hydrolysis is obtained when the concentration of the oil is 3 c.c.

#### *Effect of Enzyme Concentration on the Hydrolysis of Olive Oil*

The hydrolysis of olive oil by the three kinds of lipase was carried out using different concentrations of the enzyme and keeping other quantities constant in order to study the effect of enzyme concentration on the olive oil.

Each set of the experiments consisted of olive oil (1 c.c.), water (2 c.c.), acetate buffer (1 c.c.) and varying quantities of the enzyme lipase and incubated at 37° for 24 hours. After the period of incubation, the contents were titrated against  $N/10$ -NaOH after the addition of 25 c.c. of neutral alcohol and warming for sometime. Always a blank experiment was carried out in each case. The results are given in the following table.

TABLE VI

Oil taken = 1 c.c.				
Diff. in c.c. of $N/10$ -NaOH bet. the sample and the blank for				
Set No.	Enzyme.	castor lipase.	sesame lipase.	safflower lipase.
1	0.1 g.	36.5	3.4	2.4
2	0.2	36.7	4.2	2.7
3	0.3	37.4	5.1	3.2
4	0.4	38.3	6.5	4.5
5	0.5	44.2	7.9	6.2
6	0.6	46.8	10.2	7.8
7	0.7	49.8	11.9	10.0

From the above results, it is found that in all the three cases, the percentage hydrolysis goes on increasing as the concentration of the enzyme increases.

*Change of Activity of the Lipase on Ageing*

The hydrolysis of olive oil was carried out at different intervals of time using the three different lipases in order to study the effect of ageing on the activity of the lipase.

The hydrolysis of olive oil by lipases of the three seeds was studied from the time of preparation of the lipases up to a period of four and half months.

Each set of the experiments consisted of olive oil (1 c.c.), water (2 c.c.), lipase (0.1 g.) and acetate buffer (1 c.c.) and kept in the incubator at 37° for 20 minutes and then titrated against  $N/10$ -NaOH. The results are given in the following table.

TABLE VII  
Oil taken = 1 c.c.  
Diff. bet. the sample and the blank in terms of c.c.  
of  $N/10$ -NaOH in case of

Set No.	Time.	castor lipase.	sesame lipase.	safflower lipase.
1	0 min.	7.5	0.2	0.2
2	20 "	7.9	0.2	0.2
3	40 "	7.9	0.2	0.3
4	1 hr.	8.4	0.3	0.3
5	24 "	13.7	0.3	0.3
6	2 days	23.2	0.4	0.3
7	3	23.3	0.5	0.5
8	4	23.4	0.5	0.5
9	5	23.5	0.6	0.5
10	6	24.4	0.6	0.5
11	8	24.8	0.8	0.7
12	11	20.5	1.0	0.7
13	15	20.2	1.2	0.7
14	23	19.9	1.4	1.1
15	71	17.9	1.2	1.1
16	78	10.7	1.2	1.1
17	85	10.2	0.9	0.9
18	93	9.8	0.8	0.9
19	100	8.9	0.4	0.7
20	114	8.6	0.4	0.7
21	121	7.8	0.1	0.5
22	134	6.5	0.0	0.4
23	142	5.1	—	0.2
24	150	3.9	—	0.0
25	160	0.5	—	—

In all the three cases, the activity increases at first and then decreases on ageing and after 160 days, almost becomes zero.

From these results it appears that these lipases cannot be used for experimental purposes since their activity changes with time. So a modification was made by preparing the acetone-dried samples of these lipases. The activities of these samples were found at different intervals of time and they gave almost a constant value, for example, 1.4, 0.8 and 0.5 in terms of c.c. of  $N/10$ -NaOH in case of castor, sesame and safflower lipases respectively. So, it is advisable to use acetone-dried samples of any lipase since it keeps its activity fairly constant for an approximately long time even though it is small.

#### *Hydrolysis of Butyl Oleate by Different Lipases*

The hydrolysis of butyl oleate by different lipases was carried out in ether as the solvent. Each set of the experiments consisted of 0.018 g. mol. of ester solution, 1 g. of acetone-dried lipase of each variety, 10 c.c. of ether and a few drops of toluene kept in a corked bottle. Initially 1 c.c. of it was taken and 25 c.c. of neutral alcohol added, warmed and titrated against  $N/10$ -NaOH. This gave the blank reading. After keeping the mixture in the incubator at  $37^\circ$  at different intervals of time, 1 c.c. portion of it was taken, neutral alcohol (25 c.c.) added, warmed and titrated against  $N/10$ -NaOH. From the difference in the readings for the sample and the blank, the percentage hydrolysis was calculated. The results are tabulated below.

TABLE VIII

Percentage hydrolysis on days

Lipase.	1st.	2nd.	3rd.	4th.	5th.	6th.	7th.
1. Castor	28.0	32.0	42.0	54.0	66.0	70.0	68.0
2. Sesame	7.2	10.5	15.2	23.8	25.4	24.6	—
3. Safflower	4.1	6.5	8.9	11.2	15.3	18.1	17.4

From the results the percentage hydrolysis appears to be more in case of castor lipase and less in case of safflower lipase and the activity of the lipase appears to be in the order: castor lipase, sesame lipase and safflower lipase respectively.

So, it is found that the castor lipase is only more active.

#### C O N C L U S I O N

A general study of the lipases obtained from oil seeds with special reference to their synthetic and hydrolytic activities has been made.

The acetone-dried lipase keeps its activity fairly constant for an appreciably long time even though their activity is low. The percentage synthesis as well as the hydrolysis of esters by lipase is independent of the number of carbon atoms in the acid and only depends upon the number of carbon atoms in the alcohol.



The difference in percentage synthesis as well as hydrolysis is observed in case of normal and *iso*-esters. The percentage synthesis of the ester by lipase increases as the number of (OH) group increases in the alcohol.

The percentage synthesis of the ester is more in case of an unsaturated acid than a saturated one. The percentage synthesis of the ester is more when both the alcohol and the acid used are aromatic than when both are aliphatic. Further, the percentage synthesis is more when both alcohol and acid belong to the same family (*i.e.*, aliphatic or aromatic) than one in which they belong to different families.

The percentage synthesis of the ester by lipase increases up to a certain limit as the molecular quantity of the alcohol or acid increases till the maximum is reached.

MnSO<sub>4</sub> acts as an accelerator, whereas K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> acts as a retarder for the synthesis and hydrolysis of esters by lipase.

A comparative study of castor, sesame and safflower lipases has been made. The optimum *p*<sub>H</sub> of the lipase is independent of the nature of the buffer and the substrate but the percentage hydrolysis of the oil is more in acetate buffer and the activity of the lipase is more in its own oil.

DEPARTMENT OF BIOCHEMISTRY,  
WADIA COLLEGE, POONA.

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## ARTICLE

## RESEARCH PAPER

## APPLICATION OF MIXTURE LAW TO RHEOCHOR. PART IV

BY H. G. SILAWAT, M. V. SABNIS AND W. V. BHAGWAT

Mixture law has been found to be applicable for non-associated liquids in associated solvents over the entire range of molar fraction and at temperatures examined, i.e., 30°, 40° and 50°. The mixtures studied are toluene, benzene, chloroform and carbon tetrachloride in acetic acid, and toluene in acetone.

The application of "mixture" law to rheochor has been extended in this paper to liquid mixtures containing associated liquids in non-associated liquids. To study the applicability, the molar fraction has been varied over the whole range from 0 to 1 and because the value of rheochor varies with temperature the investigations have been carried out at different temperatures also. The following tables give our results.

$\alpha$ ,  $D$ ,  $M_m$ ,  $R_m$  and  $R_x$  have the same significance as given in previous papers (this Journal, 1949, 28, 533; 1948, 25, 165, 575 *et seq.*)

## Non-associated Liquids in Associated Solvents

TABLE I

## Toluene in acetic acid

 $R$  (acetic acid, exptl.) = 77.6.

Temp. 10°.

$\alpha$ .	$D$ .	$\eta \times 10^3$ .	$M_m$ .	$R_m$ .	$R_x$ .
0.0642	1.015	9.568	62.10	81.17	133.7
0.2052	0.9625	7.538	66.61	89.00	133.2
0.7929	0.8676	5.530	85.47	122.00	133.6

Calc. for toluene = 132.0. Obs. = 133.

Temp. = 40°.

$\alpha$ .	$D$ .	$\eta \times 10^3$ .	$M_m$ .	$R_m$ .	$R_x$ .
0.0642	1.0050	9.448	62.10	81.12	132.2
0.5052	0.9625	6.513	66.61	88.91	132.8
0.7929	0.8511	4.859	85.47	122.10	133.6

Obs. = 133.0.

Temp. = 50°.

$\alpha$ .	$D$ .	$\eta \times 10^3$ .	$M_m$ .	$R_m$ .	$R_x$ .
0.0642	0.9933	8.122	62.10	81.21	133.3
0.4800	0.8855	4.846	75.44	103.80	132.4
0.7929	0.8499	4.171	85.47	122.10	133.6

Obs. = 133.0.

TABLE II

*Benzene in acetic acid.*

Temp. = 30°.

$\alpha$ .	D.	$\eta \times 10^3$	Mm.	Rm.	R <sub>x</sub> .
0.1603	0.9933	8.519	62.94	82.83	110.4
0.3900	0.9430	6.887	67.08	90.55	110.8
0.7224	0.8964	5.822	73.06	101.50	110.9

R<sub>calc.</sub> for benzene = 109.8. R<sub>obs.</sub> = 110.6.

Temp. = 40°.

$\alpha$ .	D.	$\eta \times 10^3$	Mm.	Rm.	R <sub>x</sub> .
0.1603	0.9822	7.841	62.94	82.90	110.6
0.3900	0.9340	6.245	67.08	90.50	110.7
0.7224	0.8876	5.111	73.06	100.90	109.8

R<sub>obs.</sub> = 110.4.

Temp. = 50°.

$\alpha$ .	D.	$\eta \times 10^3$	Mm.	Rm.	R <sub>x</sub> .
0.1603	0.9716	7.112	62.94	82.80	109.0
0.3900	0.9210	5.776	67.08	99.60	110.69
0.7224	0.8798	4.939	76.06	101.40	110.6

R<sub>obs.</sub> = 110.0

TABLE III

*Chloroform in acetic acid.*

Temp. = 30°.

$\alpha$ .	D.	$\eta \times 10^3$	Mm.	Rm.	R <sub>x</sub> .
0.0819	1.074	8.986	64.00	79.49	100.4
0.2500	1.151	7.244	74.90	83.38	100.7
0.7464	1.357	5.285	104.30	94.66	100.8

R<sub>calc.</sub> for chloroform = 100.2. R<sub>obs.</sub> = 100.6.

Temp. = 40°.

$\alpha$ .	D.	$\eta \times 10^3$	Mm.	Rm.	R <sub>x</sub> .
0.0819	1.064	8.287	64.90	79.45	100.2
0.2500	1.151	6.532	74.90	83.43	100.9
0.7464	1.347	4.840	104.30	94.30	100.3

R<sub>obs.</sub> = 100.5

Temp. = 50°.

$\alpha$ .	D.	$\eta \times 10^3$	Mm.	Rm.	R <sub>x</sub> .
0.0819	1.051	7.516	64.90	79.47	100.4
0.2500	1.124	5.982	74.90	83.33	100.8
0.7464	1.334	4.537	104.30	94.44	100.5

R<sub>obs.</sub> = 100.4

TABLE IV

*Carbon tetrachloride in acetic acid,*

Temp. = 30°.

$x$	D.	$\eta \times 10^3$	Mm.	R <sub>m</sub>	R <sub>x</sub>
0.0697	1.110	10.71	66.59	80.70	122.0
0.2172	1.228	9.95	80.36	87.18	122.0
0.7482	1.533	8.94	130.20	111.60	122.8

Reals. for  $\text{CCl}_4 = 122.0$ ,  $R_{\text{obs.}} = 122.0$

Temp. = 40°.

0.0697	1.097	9.82	66.59	80.74	122.5
0.2172	1.216	8.76	80.36	87.12	121.7
0.7482	1.517	7.91	130.20	111.20	122.3

$R_{\text{obs.}} = 122.1$

Temp. = 50°.

0.0697	1.088	9.17	66.69	80.70	122.0
0.2172	1.196	8.04	80.36	87.14	122.1
0.7482	1.469	6.97	130.20	110.90	121.9

$R_{\text{obs.}} = 122.1$

TABLE V

*Toluene in acetone*

R (Acetone, exptl.) = 85.0

Temp. = 30°.

$x$	D.	$\eta \times 10^3$	Mm.	R <sub>m</sub>	R <sub>x</sub>
0.0929	0.7938	3.192	61.21	89.16	133.2
0.3674	0.8228	4.169	70.54	102.70	133.2
0.8102	0.8445	4.984	85.65	124.00	133.2

Reals. for toluene = 132.2,  $R_{\text{obs.}} = 133.1$

Temp. = 40°.

0.0929	0.7825	2.858	61.21	89.20	133.7
0.3674	0.8132	3.952	70.54	103.00	133.2
0.8102	0.8339	4.622	85.65	124.00	133.6

$R_{\text{obs.}} = 133.5$

Temp. = 50°.

0.0929	0.7714	2.564	61.21	89.26	133.2
0.3674	0.8021	3.538	70.54	103.00	133.2
0.8102	0.8241	4.467	85.65	124.80	133.1

$R_{\text{obs.}} = 133.2$

## DISCUSSION

The rheochor values for toluene in acetic acid is more or less constant over the whole range of molar concentration and also at the three temperatures 30°, 40° and 50°. The calculated value 132 is not very different from the observed value 133 (approx.). It appears therefore that the rheochor of toluene does not vary appreciably with temperature, and hence the calculated value which corresponds to boiling point is not very different from the values at lower temperatures.

Rheochor of benzene at different temperatures, as given by Friend and Hargreaves (*Phil. Mag.*, 1943, vii, 84, 644), is as follows :

Temp.	...	60°	80°	100°	140°	180°
R	...	116.4	110.4	109.8	109.8	109.2

Those results show that  $R$  varies only slightly with temperature.  $R_x$  observed by us in solution therefore at different temperatures is practically the same and not very different from the value at the boiling point (110.4). Our observed value is near about 110. It is further observed that the value is constant over the whole range of molar concentrations studied.

The results with chloroform in acetic acid and toluene in acetone are very similar.

Rheochor of  $\text{CCl}_4$  at different temperatures, as given by Friend and Hargreaves (*loc. cit.*), is given below :

Temp.	...	60°	80°	100°	140°	180°
R	...	126.0	125.3	125.1	125.2	124.2

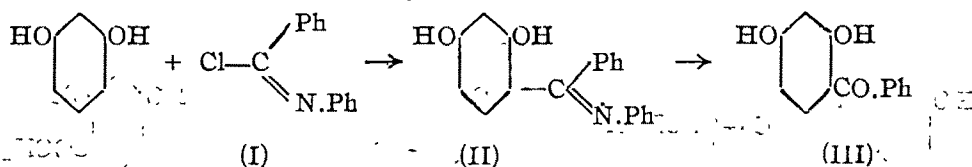
The calculated value from atomic rheochor is 122. The value we obtained is nearer about the calculated value than the value of  $R$ , given by Friend and Hargreaves (*loc. cit.*). In general therefore, we conclude that mixture law is applicable for liquid mixtures of associated and non-associated liquids over the whole range of molar concentration and at all temperatures investigated by us.

CHEMISTRY DEPARTMENT,  
HOLKAR COLLEGE,  
INDORE.

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BY (MISS) RAGINI PHADKE AND R. C. SHAH

Resorcinol, when condensed with benzanilide imidochloride (I), gave 2:4-dihydroxy-(phenylimino)benzophenone (II), identical with the product obtained by the condensation of 2:4-dihydroxybenzophenone (III) and aniline. The anil (II) easily hydrolysed to give 2:4-dihydroxybenzophenone (III). Previously Stephen (*ibid.*, 1920, 117, 1529) had directly condensed benzanilide imidochloride with resorcinol without any condensing agent, and obtained minute quantities of a product, which he considered to be the keto-anil (II), as on hydrolysis it gave 2:4-dihydroxybenzophenone (III).



The anils, which are new compounds, are coloured substances, and some are unexpectedly highly stable to acids. The hydrolysis of the anil, in general, could



case and the isolation of keto-anils of type (II), which have structural similarity to the ketimide (V), supposed to be formed during the Hoesch reaction, strongly supports the above view of the mechanism of the Hoesch reaction.

#### EXPERIMENTAL

##### *Condensation of Benzanilide Imidochloride with Resorcinol:*

##### *2:4-Dihydroxybenzophenone*

*2:4-Dihydroxy(phenylimino)benzophenone*.—To a mixture of dry resorcinol (3.5 g., 1 mol.) and benzanilide imidochloride (7.0 g., 1 mol.) in dry ether, protected from moisture, an ethereal suspension of anhydrous aluminium chloride (6.3 g., 1.5 mols.) was added drop by drop. There was a simultaneous evolution of heat and fumes of hydrogen chloride. The reaction mixture was allowed to stand for half an hour, the ether evaporated and the orange colored oil poured in ice-cold hydrochloric acid. The yellow granular solid (8.5 g.), thus obtained, was the *keto-anil* and after washing with a dilute solution of sodium bicarbonate was crystallised from hot benzene in lemon-yellow needles, m.p. 235°. (Found: N, 4.9.  $C_{15}H_{13}O_2N$  requires N, 4.8 per cent), Stephen (*loc. cit.*) gives m.p. 228-30°. It is soluble in alcohol, acetic acid, benzene and alkali. Its alcoholic solution gives a brown coloration with alcoholic ferric chloride.

*Diacetyl* derivative (acetic anhydride and pyridine) was crystallised from alcohol in white silky needles, m.p. 126-27°. (Found: C, 74.5; H, 5.4.  $C_{23}H_{19}O_4N$  requires C, 74.0; H, 5.1 per cent).

*Dibenzoyl* derivative (benzoyl chloride and pyridine) was crystallised from dilute alcohol in white needles, m.p. 163°. (Found: C, 77.4; H, 5.1.  $C_{33}H_{23}O_4N.H_2O$  requires C, 77.0; H, 4.8 per cent).

*Dimethyl ether* (methyl iodide, potassium carbonate and acetone) was crystallised from alcohol in yellow needles, m.p. 134-35°. (Found: C, 79.2; H, 5.8.  $C_{21}H_{19}O_2N$  requires C, 79.4; H, 6.0 per cent).

*Hydrolysis of the Anil*.—The anil (12.5 g.), dissolved in alcohol, was refluxed with hydrochloric acid (30 c.c.) for 3 hours. The alcohol was distilled off and the solution diluted to give a buff product (8.3 g.) which was crystallised from hot water in white needles, m. p. and mixed m. p. with an authentic sample of 2:4-dihydroxybenzophenone, 143-44°.

*2:4-Dinitrophenylhydrazone* was crystallised from alcohol in red micro-crystals, m.p. 297°. (Found: N, 13.9.  $C_{15}H_{11}O_6N_4$  requires N, 14.2 per cent).

*Condensation of 2:4-Dihydroxybenzophenone with Aniline*.—2:4-Dihydroxybenzophenone (1 g.), freshly-distilled aniline (1 g.) and powdered zinc chloride (0.7 g.), protected from moisture, were heated together in an oil-bath at 200° for half an hour. The oily mass was poured in ice-water and the solid, thus obtained, washed successively with dilute hydrochloric acid and hot water to remove unreacted aniline and ketone. It crystallised from hot benzene in lemon-yellow needles, m.p. 235°. Mixed melting point with the *keto-anil* obtained above was undepressed.



*Condensation of Benzanilide Imidochloride with Resorcinol Dimethyl Ether*  
 2:4-Dimethoxybenzophenone.—Resorcinol dimethyl ether (4.2 g., 1 mol.) and benzanilide imidochloride (6.4 g., 1 mol.) were condensed in presence of anhydrous aluminium chloride (5.5 g., 1.5 mols.) in dry ether as above. On working up the reaction mixture similarly, a yellow oil was obtained. This was extracted with ether and the extract on slow evaporation gave colorless needles (2.5 g.). On recrystallisation from dilute alcohol colorless needles of 2:4-dimethoxybenzophenone, m. p. and mixed m. p. with an authentic specimen, 83-85°, were obtained (König and Kostanecki, *Ber.*, 1906, **39**, 4028, give m. p. 87-88°; Kauffmann and Panuwetz, *ibid.*, 1910, **43**, 1207, give m. p. 83°).

Attempts were made to isolate the keto-anil formed during the reaction by carrying out the condensation at 0°, but only the ketone was obtained.

*Condensation of Benzanilide Imidochloride with Catechol*

3:4-Dihydroxybenzophenone.—Catechol (4 g.), benzanilide imidochloride (8 g.) and anhydrous aluminium chloride (7.5 g.) were refluxed in dry ether for 4 hours. On working up the reaction mixture a red oil was obtained from which the keto-anil could not be isolated in a pure state and hence it was directly hydrolysed by refluxing with alcoholic hydrochloric acid for 6 hours. On dilution, and keeping overnight at room temperature a white solid (2.4 g.) separated. It was crystallised from hot water in colorless prisms, m. p. 134°. (Rosenmund and Lohfert, *Ber.*, 1928, **61B**, 2601, give m. p. 134°).

2:4-Dinitrophenylhydrazones was crystallised from acetic acid in red micro-needles, m. p. 282° (decomp.). (Found: N, 14.3.  $C_{18}H_{14}O_6N_4$  requires N, 14.2 per cent).

*Condensation of Benzanilide Imidochloride with Orcinol:*

2:4-Dihydroxy-6-methylbenzophenone

2:4-Dihydroxy-6-methyl(phenylimino)benzophenone.—Anhydrous orcinol (3 g.) and benzanilide imidochloride (6 g.) were condensed in presence of anhydrous aluminium chloride (5.2 g.) in dry ether as usual. The orange solid obtained on working up the reaction mixture was the hydrochloride of the keto-anil. As it could not be crystallised, it was directly hydrolysed to the anil by treating its alcoholic solution with sodium bicarbonate. On dilution the anil separated as a sticky cream-coloured solid and was crystallised from a mixture of ether and petroleum in colorless rhomboid needles, m. p. 102-104° (decomp.). (Found: N, 4.3.  $C_{20}H_{17}O_2N$  requires N, 4.6 per cent). Its alcoholic solution gave a faint orange coloration with alcoholic ferric chloride.

The hydrochloride was prepared by passing gaseous hydrogen chloride into an ethereal solution of the anil, m. p. 264°. (Found: N, 3.8; Cl, 10.5.  $C_{20}H_{17}O_2NCl$  requires N, 4.1; Cl, 10.3 per cent).

*Hydrolysis of the Anil.*—The anil (5 g.) was hydrolysed by refluxing with alcoholic hydrochloric acid when on working up as usual, 2:4-dihydroxy-6-methylbenzophenone,

was obtained. It was crystallised from hot water in colorless needles (1 g.), m.p.  $141^{\circ}$ . Hoesch (*Ber.*, 1915, **48**, 1130) gives the same m.p. Its alcoholic solution gave a brown-red coloration with alcoholic ferric chloride.

2: 4-*Dinitrophenylhydrazone* separated as red micro-crystals, m.p.  $226^{\circ}$ . (Found: N, 14.0.  $C_{20}H_{16}O_6N_4$  requires N, 13.7 per cent).

*Condensation of Benzanilide Imidochloride with Resacetophenone*

2-Benzoyl-4-acetylresorcinol.—To a mixture of resacetophenone (4 g.) and benzanilide imidochloride (6.2 g.), anhydrous aluminium chloride (6 g.), dissolved in dry nitrobenzene, was added gradually. After keeping at room temperature for half an hour the contents, protected from moisture, were heated for 6 hours at  $95-100^{\circ}$  when hydrogen chloride was evolved. The dark oil was poured in ice-cold hydrochloric acid. After removal of the nitrobenzene by steam-distillation, the residue in the flask was dissolved in sodium hydroxide (10%, 150 c.c.) and filtered to remove the insoluble benzanilide (3.3 g.). The filtrate on acidification gave a chocolate coloured product (1.6 g.) which was washed with hot water to remove the unreacted resacetophenone. It was extracted with petroleum ether and the residue crystallised repeatedly from 50% alcohol (charcoal) in colorless needles, m.p. and mixed m.p. with an authentic specimen of 2-benzoyl-4-acetylresorcinol,  $167-68^{\circ}$ . (Found: C, 70.0; H, 4.9. Calc. for  $C_{18}H_{12}O_3$ : C, 70.1; H, 4.7 per cent). (Desai and Vakil, *Proc. Ind. Acad. Sci.*, 1940 **12A**, 394, give m.p.  $165^{\circ}$ ). Its alcoholic solution gave a deep red coloration with alcoholic ferric chloride.

*Condensation of Benzanilide Imidochloride with Phloroglucinol:*

2:4:6-Trihydroxybenzophenone

2:4:6-Trihydroxy(phenylimino)benzophenone.—Anhydrous phloroglucinol (4 g.) was condensed with benzanilide imidochloride (7.2 g.) in presence of anhydrous aluminium chloride (6.4 g.) in dry ether, as usual. The yellow anil (8 g.) obtained was washed with a sodium bicarbonate solution and crystallised from alcohol in yellow needles, m.p.  $191^{\circ}$  (decomp.). (Found: N, 4.7.  $C_{19}H_{13}O_5N$  requires N, 4.5 per cent). Its alcoholic solution gave no coloration with alcoholic ferric chloride.

*Triacetyl derivative* (acetic anhydride and concentrated sulphuric acid) was crystallised from alcohol in yellow needles, m.p.  $115-16^{\circ}$  (Found: C, 69.7; H, 5.0.  $C_{28}H_{21}O_6N$  requires C, 69.6; H, 4.9 per cent).

*Tribenzoyl derivative* (benzoyl chloride and pyridine) was crystallised from benzene after adding petroleum ether in yellow needles, m.p.  $182^{\circ}$ . (Found: C, 77.8; H, 4.8.  $C_{30}H_{27}O_3N$  requires C, 77.8; H, 4.4 per cent).

*Trimethyl ether* (dimethyl sulphate, potassium carbonate and acetone) was crystallised from alcohol (50%) in colorless, glistening plates, m.p.  $148-50^{\circ}$ . (Found: C 76.4; H, 5.2.  $C_{22}H_{21}O_3N$  requires C, 76.1; H, 5.4 per cent).

*Hydrolysis of the Anil.*—The anil (6 g.) was hydrolysed by refluxing with alcoholic hydrochloric acid for 4 hours. The oil obtained was extracted with ether, ether eva-

porated and the product crystallised from hot water in yellow silky needles (1.8 g.), m.p. and mixed m.p. with an authentic sample of 2:4:6-trihydroxybenzophenone, 165° (Hoesch, *Ber.*, 1915, **48**, 1130, give the same m.p.).

#### *Condensation of Benzanilide Imidochloride with Pyrogallol*

2:3:4-Trihydroxybenzophenone.—Pyrogallol (4 g.) was condensed with benzanilide imidochloride (6.1 g.) in presence of anhydrous aluminium chloride (5.6 g.) by refluxing in dry ether for 4 hours. The crude anil obtained, as an oil after working up the reaction mixture as usual, could not be isolated in a pure state and was directly hydrolysed to the ketone (2.3 g.) with alcoholic hydrochloric acid. 2:3:4-Trihydroxybenzophenone obtained was crystallised from hot water in colorless needles, m.p. 140-41° (Fischer and Rapaport, *Ber.*, 1913, **46**, 2393 give the same m.p.). Its alcoholic solution gave a dark coloration with alcoholic ferric chloride.

The condensation was also carried out on a steam-bath (2 hours) with nitrobenzene as a solvent. The yield, however, was reduced and the product was accompanied with some tarry material.

2:4-Dinitrophenylhydrazone was crystallised from acetic acid in small shining orange needles, m.p. 237° (decomp.). (Found: N, 13.6.  $C_{10}H_6O_7N_4$  requires N, 13.7 per cent).

#### *Condensation of Benzanilide Imidochloride with Phenol*

*p*-Hydroxybenzophenone.—To a mixture of phenol (2.5 g.) and benzanilide imidochloride (4.6 g.) powdered anhydrous aluminium chloride (4.5 g.) was added. After the initial reaction, the mixture, protected from moisture, was heated for 12 hours at 120°-130° during which fumes of hydrogen chloride were evolved. The orange solid was crushed and added to ice-cold hydrochloric acid. The yellow solid obtained was directly crystallised from dilute acetic acid in colorless needles (1.1 g.), m.p. 134-35° (Doebner and Stackmann, *Ber.*, 1877, **10**, 1969, give m.p. 134°).

When this condensation was carried out under the usual conditions using ether as a solvent, quantitative yield of phenyl benzoate was obtained; while in nitrobenzene at 160° (6 hours) a tarry mass resulted from which nothing could be isolated.

*Acetyl derivative* was crystallised from dilute alcohol in colorless silky needles, m.p. 82°. Doebner and Stackmann (*loc. cit.*) give m.p. 81°.

*Condensation of Benzanilide Imidochloride with Anisole: p*-Hydroxybenzophenone.—A mixture of anisole (2.5 g.), benzanilide imidochloride (5.2 g.) and anhydrous aluminium chloride (5 g.) was heated for 5 hours at 130°-140°. The solid obtained on addition to ice-cold hydrochloric acid was refluxed with alcoholic sodium hydroxide (10%) for 6 hours. The alcohol was distilled off and the solution acidified to give a white pasty product. It was crystallised from dilute acetic acid in colorless needles (2 g.), m.p. 134°. Mixed m.p. with a sample of *p*-hydroxybenzophenone obtained above was undepressed.

Low yields were obtained when the condensation was carried out in boiling ether (4 hours); while in nitrobenzene at 130° (4 hours) a pasty product was obtained which could not be crystallised.

*Condensation of Benzanilide Imidochloride with  $\alpha$ -Naphthol :**1-Hydroxy-4-benzoylnaphthalene*

*1-Hydroxy-4-(phenylimino)benzoylnaphthalene*.— $\alpha$ -Naphthol (4.4 g.) was condensed with benzanilide imidochloride (6.6 g.) in presence of anhydrous aluminium chloride (6.0 g.) in dry ether as usual. The orange solid obtained on working up the reaction mixture was the anil hydrochloride (10.9 g.). It was hydrolysed with sodium bicarbonate and the anil crystallised from toluene in chocolate coloured granules, m.p. 172-74°. (Found : N, 4.1.  $C_{23}H_{17}ON$  requires N, 4.3 per cent). The anil is soluble in alcohol, acetic acid, alkali, benzene and toluene. Its alcoholic solution gave no coloration with alcoholic ferric chloride.

The *hydrochloride* separated as orange micro-crystals, m.p. 265-68°. (Found : Cl, 10.6.  $C_{23}H_{17}ONCl$  requires Cl, 10.3 per cent).

*Acetyl derivative* was crystallised from a mixture of ether and petroleum ether in buff coloured needles, m.p. 154°. (Found : N, 3.8.  $C_{25}H_{19}O_2N$  requires N, 3.8 per cent).

*Benzoyl derivative* was crystallised from benzene after adding petroleum ether, in colorless needles, m.p. 181°. (Found : N, 3.4.  $C_{30}H_{21}O_2N$  requires N, 3.3 per cent).

*Hydrolysis of the Anil*.—The hydrolysis of the anil could not be carried out under the usual conditions. Even with concentrated potassium hydroxide solution (50%) in a sealed tube at 180°-200° for 8 hours the original compound was recovered ; and with acetic acid and concentrated hydrochloric acid in a sealed tube at 150° for 10 hours only traces of the ketone (m.p. 158-60°) were obtained. Hence the following method was followed for hydrolysis.

The anil (2.4 g.) was dissolved in a minimum quantity of acetic acid and heated with sulphuric acid (40%, 6.2 c.c.) at 130° for 3 hours. On dilution, the ketone separated and it was crystallised from alcohol in golden yellow needles, m.p. 164-65°, yield 0.52 g. Scholl and Seer (*Annalen*, 1912, 394, 151) give the same m.p.

*2:4-Dinitrophenylhydrazone* crystallised from alcohol as red micro-needles, m.p. 285° (decomp.). (Found : N, 12.5.  $C_{23}H_{16}O_6N_4$  requires N, 12.5 per cent.).

*Condensation of Benzanilide Imidochloride with  $\beta$ -Naphthol :**2-Hydroxy-1-benzoylnaphthalene*

*2-Hydroxy-1-(phenylimino)benzoylnaphthalene*.— $\beta$ -Naphthol (2.4 g.) was condensed with benzanilide imidochloride (6.3 g.) in presence of anhydrous aluminium chloride (5.9 g.) in dry ether as usual. The orange anil hydrochloride obtained on working up the reaction mixture, was converted into the free anil as above. The anil was crystallised from 50% alcohol in yellow needles, m.p. 178°-79°. (Found : N, 4.6.  $C_{23}H_{17}ON$  requires N, 4.3 per cent). It is soluble in alcohol, acetic acid, alkali, benzene and acetone but sparingly soluble in ether. Its alcoholic solution gave a feeble orange coloration with alcoholic ferric chloride.

The *hydrochloride* separated as orange shining plates, m.p. 270°. (Found : N, 3.9 ; Cl, 10.1.  $C_{23}H_{17}ONCl$  requires N, 3.9 ; Cl, 10.3 per cent).

*Acetyl derivative* crystallised from alcohol in tiny, pale yellow needles, m. p. 137-38°. (Found : N, 4.5.  $C_{25}H_{19}O_2N$  requires N, 4.1 per cent).

*Benzoyl derivative* was crystallised from a mixture of benzene and petroleum ether in yellow needles, m.p. 146-47°. (Found : N, 3.7.  $C_{30}H_{21}O_2N$  requires N, 3.3 per cent).

*Hydrolysis of the Anil.*—Attempts to hydrolyse the anil with alcoholic potassium hydroxide or hydrochloric acid, potassium hydroxide in glycerine, or with concentrated sulphuric acid were unsuccessful, and hence the following method was adopted.

The anil (4 g.) was heated with aqueous potassium hydroxide (50%, 20 c.c.) in a sealed tube at 130°-135° for 5 hours. The solution was then diluted and acidified when a golden yellow solid (2.2 g.) separated. This was repeatedly crystallised from dilute alcohol (25%) when 2-hydroxy-1-benzoylnaphthalene was obtained in pale yellow needles, m.p. 140-41°. Perrier (*Compt. rend.*, 1893, 116, 1141) gives m.p. 141°.

#### *Attempted Condensation of Benzanilide Imidochloride with Hydroquinone*

Hydroquinone (4.6 g.) and benzanilide imidochloride (9.2 g.) in ethereal solution were mixed with an ethereal solution of anhydrous aluminium chloride (15.7 g., 2.2 mols.) and worked up as usual. On crystallisation the product was found to be quinol monobenzoate, m.p. 61-62° (9.7 g.). Will and Johnson (*Ber.*, 1893, 26, 1909) give m.p. 62-63°. With benzoyl chloride and pyridine it gave hydroquinone dibenzoate, m.p. and mixed m.p. with an authentic specimen, 200-201°. Doebner (*Annalen*, 1881, 210, 263) gives m.p. 199°.

Attempts at this condensation using nitrobenzene as a solvent or without a solvent also resulted in the formation of hydroquinone monobenzoate.

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ORGANIC CHEMISTRY LABORATORY,  
ROYAL INSTITUTE OF SCIENCE,  
BOMBAY.

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# ON THE PREPARATION OF BACTERICIDALS FROM ORGANO-MERCURIALS. PART I

BY S. S. GUHA SIRCAR AND SACHINDRA KUMAR DATTA

Twenty-seven organo mercurials, derived from phenoxyacetic acid and phenylglycine-*o*-carboxylic acid of which 7 are known and 20 unknown, were prepared and analysed. Bactericidal activity of 22 of these compounds against *B. Coli* and *B. Para Typhosus B* was tested. All these compounds have been found to have a fair, and some quite high, germicidal potency.

Though about a dozen organo-mercury compounds like Mercurochrome, Merbaphen, Mersalyl, Metaphen and Mercurin are being widely used in medical practice, a systematic investigation of the simpler organo-mercurials does not seem to have been undertaken. It is proposed to describe in this and the following papers of this series, the preparation, properties and bactericidal action against *B. Coli* and *B. Para Typhosus B*, of a number of mercurated phenols, amines, urea, sulphanilamide derivatives and azo dyes, which have already been prepared and investigated in the laboratories of the Dacca University and of the Ravenshaw College, Cuttack. The first paper relates to a number of mercurated phenoxyacetic acids and phenylglycine-*o*-carboxylic acids, which were chosen in the belief that the protected phenolic and aminic groups in these molecules would lead to products of very low toxicity and of very high stability towards air and light, as well as towards body fluids.

In this paper, 22 aryloxy-fatty acids have been mercurated by standard methods; only seven of these are mentioned in the literature (D.R.P., 261299; 264,267; 261,875; vide also Goordon and Kipins, U.S.P., 1914, No. 2343,549). Their properties, and in some cases even their melting points, are not described. Only one method for their preparation is mentioned, whereas 4 methods of mercuration have been described in this paper. Five new mercury compounds of phenylglycine-*o*-carboxylic acid are also described, the products have been proved to be fairly stable to air and light and towards dilute acids and alkalis, very dilute  $H_2S$  and 1% NaCl solutions, which occur in the body fluids. Their solubility in dilute NaOH in the cold to give nearly neutral solutions ( $p_H$  7 to 7.8) gives them an additional advantage in actual use.

TABLE I

*Bactericidal action of mercury compounds of aryloxy-fatty acid series.*

Temp. = 29.  $p_H$  = 7 to 7.6. After 12½ minutes.

No. of Compound.	Max. effective dilution against		No. of Compound.	Max. effective dilution against	
	<i>B. Coli.</i>	<i>B. Para Typhosus B.</i>		<i>B. Coli.</i>	<i>B. Para Typhosus B</i>
1	1: 10,000	1: 10,000	13	1: 50,000	1: 40,000
2	1: 15,000	1: 15,000	14	1: 45,000	1: 38,000
3	1: 15,000	1: 15,000	15	1: 50,000	1: 40,000
4	1: 15,000	1: 15,000	16	1: 45,000	1: 38,000
8	1: 45,000	1: 38,000	17	1: 170,000	1: 130,000
9	1: 40,000	1: 40,000	18	1: 20,000	1: 20,000
10	1: 40,000	1: 40,000	19	1: 40,000	1: 25,000
11	1: 60,000	1: 50,000	20	1: 65,000	1: 50,000
12	1: 75,000	1: 60,000			

TABLE II

*Bactericidal action of the mercury compounds of phenylglycine-o-carboxylic acid.*Temp. = 29°.  $p_H = 7.5$ .

No.	After X mins.	Maximum effective dilution against	
		B. Coli.	B. Para Typhosus B.
23	12½ mins	1: 800,000	1: 150,000
24	"	1: 200,000	1: 100,000
25	"	1: 1000,000	1: 500,000
	3 hrs	1: 1000,000	—
26	12½ mins.	1: 500,000	1: 200,000
27	"	1: 2000,000	1: 700,000

## E X P E R I M E N T A L

*Preparation of Aryloxy-fatty Acids.*—The general method of preparation of aryloxy-fatty acids from the appropriate phenol and chloro- or iodo-fatty acid (*J. Amer. Chem. Soc.*, 1931, 53, 304; 1943, 65, 1555) was adopted with a slight modification. The aryloxy-acids obtained as oils (which soon solidified) were directly crystallised from hot water, until no further change could be seen in their melting points. By this process of purification, the substances obtained were pure enough, as was established from their equivalent weight determinations (0.1 g. of the acid, dissolved in 10 c.c. of alcohol, was titrated against  $N/10$ -NaOH solution) and a comparison of the m.p. with those given in the literature (Table III). In general, these melting points obtained were similar to those previously reported. In some cases somewhat higher melting points were obtained.

TABLE III

Acid.	M.p. (obs.)	M.p. (lit.).	Equivs. (obs.).	Equivs. (calc.).
1. Phenoxy-acetic acid		96-97°, 98-99.1°	152.8	152
2. <i>o</i> -Cresoxy-		151-52°, 156.8-157.4°	167	166
3. <i>m</i> -Cresoxy-		102-103°, 103-103.5°	167.56	166
4. <i>p</i> -Cresoxy-		134-36°, 138.2-138.7°	166.68	166
5. <i>o</i> -Nitrophenoxy-		156.5°, 158.2-158.5°	197.85	197
6. <i>m</i> -Nitrophenoxy-		151-54.5°, 156.4-156.7°	195.8	197
7. <i>p</i> -Nitrophenoxy-		184°, 187.2-187.5°	196.25	197
8. <i>o</i> -Chlorophenoxy-		143-45°, 147.2-147.7°	186	186.5
9. <i>m</i> -Chlorophenoxy-		108-10°, 100.7-110.2°	185.2	186.5
10. <i>p</i> -Chlorophenoxy-		156.7-157.2°, 155-156.5°	185.6	186.5
11. $\alpha$ -Naphthoxy-		191-92°	200.5	202
12. $\beta$ -Naphthoxy-		153-54.5°	201	202
13. <i>o</i> -Xylenoxy-	161-62°	—	181.82	180
14. <i>m</i> -Xylenoxy-	111°	—	181.50	180
15. Guaiacoxy-		121.4°	181.68	182
16. Thymoxy-		148-49°	206.9	208
17. <i>p</i> -Iodophenoxy-		154-56°, 159.5-60°	276.8	277.93
18. $\beta$ -Phenoxy-propionic acid	96-97°	—	166.8	166
19. $\beta$ - <i>o</i> -Cresoxy		94.5°	180.8	180
20. $\beta$ -Guaiacoxy-	134-35°	—	195.66	196
21. <i>o</i> -Nitrophenoxy-		121-22°	210.02	211
22. <i>p</i> -Nitrophenoxy-		118-19°	211.83	211

*Mercuriation of Aryloxy-fatty Acids.*—The following mixtures of solutions were heated on a water-bath until a test portion became entirely soluble in alkali (about 4-6 hours):—

(a) One mol. of yellow mercuric oxide in sufficient 50% acetic acid to dissolve it, and one mol. of aryloxy-fatty acid in 50% alcoholic solution.

(b) Equimolecular amounts of mercuric oxide and aryloxy-fatty acid in aqueous medium were heated on a water-bath with occasional stirring till the yellow colour changed to white.

(c) Equimolecular quantities of mercuric acetate in water and aryloxy-fatty acid in dilute acetic acid solution.

(d)  $\text{HgO}$ , freshly precipitated from  $\text{HgCl}_2$ , was mixed with an alkaline solution of the aryloxy fatty acid.

In (a), (b) and (c), the products were separated as powdery substance and in (d) dilution with water and acidification with dilute acetic acid were required. The phenoxy and cresoxy compounds were formed easily within 45 minutes, chloro compounds required at least an hour, while xylenoxy compound came out almost immediately. To obtain the compound of  $\alpha$ -naphthoxyacetic acid heating was controlled between  $60^\circ$  and  $70^\circ$  for 30 minutes; the filtration and subsequent purification being done very quickly. Longer heating and exposure to light and air made the compound dark in colour. *p*-Nitrophenoxypropionic acid derivative came out with a small yield after 6 hours' heating and on pouring the mixture in a large volume of cold water and after standing overnight.

An attempt was made to mercurate them with mercuric chloride, but it failed.

*Purification.*—The substances were dissolved in dilute alkali and were reprecipitated either by dilute acetic acid or by  $\text{CO}_2$ , or a solution of the substance in hot glacial acetic acid was poured in a large volume of cold water. The precipitate was filtered, washed with hot water, boiled with alcohol and filtered hot and dried.

*General Properties.*—All the compounds are insoluble in water, in dilute acids and in most organic solvents, but are soluble in glacial acetic acid. They are easily soluble in dilute alkali. Conc.  $\text{HCl}$  decomposes them to mercuric chloride and the corresponding aryloxy-fatty acid. From solutions of the compounds in  $\text{KI}$ , by adding requisite amount of dilute  $\text{H}_2\text{SO}_4$ , iodo-mercury compounds may be formed. The compounds dissolve in iodine in  $\text{KI}$ , but break down on the addition of  $\text{H}_2\text{SO}_4$  to mercuric iodide and iodo-phenoxyacetic acid. The methyl ester of hydroxymercuriphenoxyacetic acid can be easily obtained.  $\text{Cu}$ ,  $\text{Zn}$ ,  $\text{Fe}$ ,  $\text{Ni}$  and  $\text{Al}$  salts are easily thrown down, being insoluble. They are also insoluble in dilute  $\text{HCl}$ , but break down when boiled with  $\text{HCl}$  to insoluble phenoxyacetic acid,  $\text{HgCl}_2$  and the metallic chloride. Almost all of the compounds are stable to ammonium sulphide and hydrogen sulphide at the ordinary temperatures.

*Mercuriation of Phenylglycine-o-carboxylic Acid.*—Anthranilic acid (13.6 g.), chloroacetic acid (11.4 g.) and sodium carbonate (anhyd., 17 g.) in 100 c.c. water were heated on a water-bath for 3 hours, cooled and acidified with dilute  $\text{HCl}$ . A light brown precipitate of phenylglycine-o-carboxylic acid was obtained, which was filtered next day, recrystallised from water to get colorless crystals, m.p.  $209^\circ$ .



The mono- and diacetoxymercury compounds were prepared from HgO and dilute acetic acid; the nitro compounds with mercuric nitrate in aqueous solution and the Cl-Hg compounds were prepared by the method of Neogi and Chatterjee (this *Journal*, 1928, 5, 221) by HgCl<sub>2</sub> in presence of sodium bicarbonate; use of glycerol was not necessary here. All the compounds are insoluble in water, in acids and in most organic solvents, but are soluble in alkali.

The equivalents of the compounds were determined and Hg was estimated by Whitmore's gold crucible method (Whitmore, "Organic Compounds of Mercury," p. 365, 1921) and chlorine was determined by Piria and Schiff's method. The results of the analysis show that in all cases mono-mercurated anhydride of aryloxy-fatty acids, were formed.

*Bacterical Tests.*—The Rideal Walker Drop method (*Lancet*, 1909, ii, 1516; *J. Roy. Sant. Inst.*, 1903, 424) was followed in determining the bactericidal action of the compounds prepared. The results are shown in Table III and Table IV.

TABLE IV  
Analysis of the mercury compounds.

Name of derivatives.	M p.	Equiv.		%Hg.		%Chlorine	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
1. C <sub>6</sub> H <sub>4</sub> (-O-CH <sub>2</sub> COO)-Hg	230° (decomp.)	350	351.5	57.1	56.55		
2. CH <sub>3</sub> .C <sub>6</sub> H <sub>3</sub> (-O-CH <sub>2</sub> COO)-Hg (o)	243° (brown)	364	365.2	54.8	55		
3. CH <sub>3</sub> .C <sub>6</sub> H <sub>3</sub> '(-O-CH <sub>2</sub> COO)-Hg (m)	200-202° (black)	364	364.8	54.8	55.2		
4. CH <sub>3</sub> .C <sub>6</sub> H <sub>3</sub> '(-O-CH <sub>2</sub> COO)-Hg (p)	158° (brown)	364	354.92	54.8	53.9		
5. NO <sub>2</sub> .C <sub>6</sub> H <sub>3</sub> '(-O-CH <sub>2</sub> COO)-Hg (o)	215° (decomp.)	395	—	50.6	51		
6. NO <sub>2</sub> .C <sub>6</sub> H <sub>3</sub> '(-O-CH <sub>2</sub> COO)-Hg (m)	162° (brown liq.)	395	—	50.6	49.8		
7. NO <sub>2</sub> .C <sub>6</sub> H <sub>3</sub> '(-O-CH <sub>2</sub> COO)-Hg (p)	181° (,,)	395	—	50.6	51.81		
8. Cl.C <sub>6</sub> H <sub>3</sub> (-O-CH <sub>2</sub> COO)-Hg (o)	226° (decomp.)	384.5	385.6	52	51.68		
9. Cl.C <sub>6</sub> H <sub>3</sub> (O-CH <sub>2</sub> COO)-Hg (m)	215° (,,)	384.5	383.9	52	51.05		
10. Cl.C <sub>6</sub> H <sub>3</sub> (O-CH <sub>2</sub> COO)-Hg (p)	247° (brown)	384.5	384.85	52	52.8		
11. C <sub>10</sub> H <sub>6</sub> (O-CH <sub>2</sub> COO)-Hg (α)	230-32° (black)	400	398.82	50	48.6		
12. C <sub>10</sub> H <sub>6</sub> (-O-CH <sub>2</sub> COO)-Hg (β)	204° (decomp.)	400	400.65	50	49.1		
13. (CH <sub>3</sub> ) <sub>2</sub> .C <sub>6</sub> H <sub>3</sub> (O-CH <sub>2</sub> COO)-Hg (o)	26 (brown)	379	378.5	52.7	51.92		
14. (CH <sub>3</sub> ) <sub>2</sub> .C <sub>6</sub> H <sub>3</sub> (O-CH <sub>2</sub> COO)-Hg (m)	140° (liq.)	379	378.81	52.7	51.36		
15. CH <sub>3</sub> O.C <sub>6</sub> H <sub>3</sub> (O-CH <sub>2</sub> COO)-Hg	222° (brown)	380	381.4	52.63	52.9		
16. (CH <sub>3</sub> -CH.C <sub>6</sub> H <sub>3</sub> 'O-CH <sub>2</sub> COO)-Hg	232° (,,)	406	406.58	49.3	50.01		
17. I.C <sub>6</sub> H <sub>3</sub> (O-CH <sub>2</sub> COO)-Hg (p)	251-52° (decomp.)	475.9	474.86	42.01	41.06		
18. C <sub>6</sub> H <sub>4</sub> (-O-CH <sub>2</sub> -CH <sub>2</sub> COO)-Hg (β)	194-95° (brown)	364	364.86	54.8	53.1		
19. CH <sub>3</sub> .C <sub>6</sub> H <sub>3</sub> (-O-CH <sub>2</sub> -CH <sub>2</sub> COO)-Hg (o)	232° (brown)	378	379.29	52.9	51.82		
20. CH <sub>3</sub> O.C <sub>6</sub> H <sub>3</sub> O-CH <sub>2</sub> -CH <sub>2</sub> COO)-Hg	151° (decomp.)	394	393.05	50.76	51.6		
21. NO <sub>2</sub> .C <sub>6</sub> H <sub>3</sub> O-CH <sub>2</sub> -CH <sub>2</sub> COO)-Hg (o)	210° (,,)	409	—	48.89	49.46		
22. NO <sub>2</sub> .C <sub>6</sub> H <sub>3</sub> O-CH <sub>2</sub> -CH <sub>2</sub> COO)-Hg (p)	235°	409	—	48.89	47.62		
23. Acetoxy-Hg-phenylglycine- <i>o</i> -carboxylic acid	270°	437	—	45.76	45.14		
24. Diacetoxy-,,	225°	679	—	58.91	58.01		
25. Chloro-,,	236°	429.5	—	46.56	47.03	8.26	8.75
26. Dichloro-,,	196-93°	664	—	60.24	59.86	10.71	10.18
27. Nitro-,,	215°	456	—	43.85	44.03	—	—

ORGANIC CHEMISTRY LABORATORY,  
DACCA UNIVERSITY,  
DACCA, EAST PAKISTAN.

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## STUDIES ON CARBON MONOXIDE AND CARBON MONOXIDE-HYDROGEN MIXTURES UNDER SILENT ELECTRIC DISCHARGE: INFLUENCE OF TEMPERATURE AND GAS PRESSURE

BY R. H. SAHASRABUDHEY AND S. M. DRSHPANDE

Results for (a) CO and (b) CO-H<sub>2</sub> mixtures in silent discharge by 3 to 9 kV of 500 cycles, in 100 to 400 mm. showed a maximum pressure reduction ( $\Delta p$ ) of about 17%, followed by a steady state. Initial pressure rise and temperature fall decrease  $\Delta p$  in (a) and increase it in (b). Initial  $\Delta p$  corresponds to 'second order reaction' associated with H.CHO formation in (b). 'First order' constants are observed in (a) near the steady state due to dissociation of the suboxide complex and ionic clusters

The behaviour of carbon monoxide has been studied under silent electric discharge by Brodie (*Proc. Roy. Soc.*, 1873, **21**, 245; *Ann. Physik*, 1873, **169**, 270; *Ann. chim. Pharm.*, 1873, **169**, 270), Berthelot (*Compt. rend.*, 1906, **142**, 533; *Ann. chim. phys.*, 1906, *viii*, 9, 173), Ott (*Ber.*, 1925, **68**, 772), Crespi and Lunt (*J. Chem. Soc.*, 1925, 2052). Formation of CO<sub>2</sub> and the ill defined 'carbon suboxides' has been reported. In the case of CO-H<sub>2</sub> mixtures studied by Losanitsch (*Ber.*, 1911, **44**, 312), Löb (*Ber.*, 1904, **37**, 3593), Wendt and Evans (*J. Amer. Chem. Soc.*, 1928, **50**, 2610) and Koenig and Wenig (*Festschrift 100-Jahr. Bestehen, Tech. Hochschule zu Karlsruhe*, 1925, p. 525), the formation of a number of products amongst them CO<sub>2</sub>, H.CHO, H.COOH, CH<sub>2</sub>OH.CHO etc. has been reported. No attempt, however, appears to have been made, excepting one by Caress and Rideal (*Proc. Roy. Soc.*, 1928, **A**, **120**, 370) in the case of CO-H<sub>2</sub> interaction, at elucidating the mechanism and kinetics of these reactions. In view of the earlier work of the authors (under publication) a re-examination of the above systems appeared of interest. The influence of temperature and of gas pressure has been investigated.

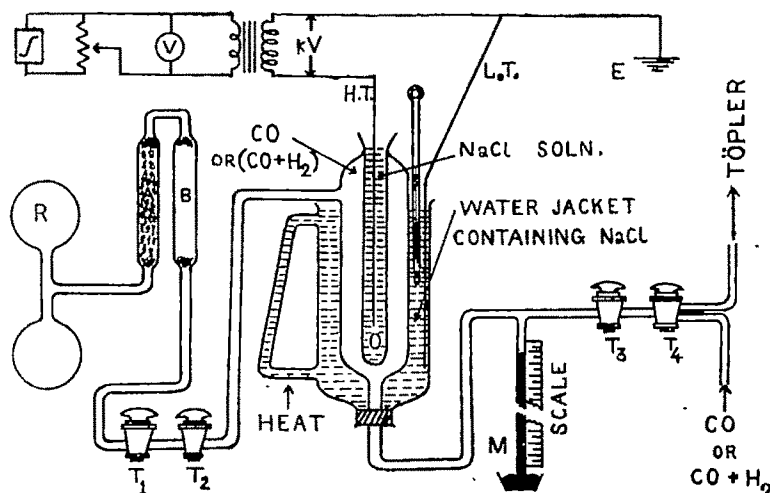
### EXPERIMENTAL

The general arrangement of the apparatus and electrical connections are shown in Fig. 1. The apparatus in its essentials consists of an all-glass Siemens' ozoniser O, a manometer M to note the pressure variations and a reservoir R to store the gases, all connected in series. The two stoppers T<sub>1</sub> and T<sub>2</sub>, in between the ozoniser and the reservoir, serve the purpose of admitting and regulating the gas to the ozoniser at any desired pressure. The system is connected to a Töpler through two glass stoppers T<sub>3</sub> and T<sub>4</sub> by means of which vacuum could be created in the ozoniser. This last is surrounded with a water jacket which can be heated to any desired temperature.

By connecting T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub>, T<sub>4</sub> to the Töpler vacuum was created inside the whole system. Carbon monoxide, prepared separately by the action of hot concentrated sulphuric acid on oxalic acid and freed from CO<sub>2</sub> or its mixture with H<sub>2</sub>, was admitted into the reservoir R through T<sub>4</sub> and the drying tubes A and B containing phosphorus pentoxide and anhydrous calcium chloride respectively. By suitably working the stop-

cocks and the Töpler it was possible to admit gas in the ozoniser at any desired pressure. Investigations were carried out with carbon monoxide at about 190, 260, 320 and 380 mm. pressure and at 25°, 40°, 50°, 70° and 80°. In the case of carbon monoxide-hydrogen mixtures (1:1 by volume) the reaction was studied at about 140, 195, 260 and 380 mm. initial gas pressure and at 30°, 50° and 70°.

Fig. 1



The ozoniser was excited by an A.C. supply of 500 cycles frequency obtained by means of a 2kVA motor alternator set worked off 220 volt D.C. mains, and at appropriate applied potentials corresponding to a constant  $(V - V_m)$  (Joshi, *Curr. Sci.*, 1939, 8, 548).

The progress of the reaction was followed by observing the pressure variation at 2, 5, 10, 15, 20, 30, 45, 60, 75.....etc. minutes till a steady state (equilibrium) was reached when no further sensible change in pressure was observed. The results are shown in Tables I and II and graphically in Figs. 2, 3 and 4.

For considerations of space all the observations relating to the time variation of pressure at different temperatures and pressures have not been included here. A typical set of observations with CO and a mixture of CO-H<sub>2</sub>, however, has been represented graphically in Figs. 2, 3 and 4. Tables I and II show the influence of initial gas pressure and temperature on the progress of the reaction in CO and CO-H<sub>2</sub> respectively.

It will be seen (vide Figs. 2 and 3) that in either case, there is during the course of the discharge a progressive reduction in the gas pressure till a final steady state is reached. It is interesting, however, to observe that while in the case of CO-H<sub>2</sub> mixtures a rise in the initial pressure has a favourable effect on the change, as indicated by percentage decrease in the pressure (Table II, column 3, Fig. 4), in the case of CO it has an adverse effect (Table I, column 3 and Fig. 4).

A rise in temperature of the ozoniser accelerates the reaction in the case of CO as evinced by a decrease in the time required for reaching the equilibrium as well as by an increase in the extent of the change (Table I, columns 4 and 3, Fig. 2).

TABLE I  
*Carbon monoxide : Influence of initial gas pressure and temperature.*

No.	Applied potential (kV).	40°				50°				70°				80°			
		Initial pres- sure (mm.)	Total fall in pres- sure (mm.)	% Re- duction in pres- sure.	Time reqd. to reach equilib. (min.)	Initial pres- sure (mm.)	Total fall in pres- sure (mm.)	% Re- duction in pres- sure.	Time reqd. to reach equilib. (min.)	Initial pres- sure (mm.)	Total fall in pres- sure (mm.)	% Re- duction in pres- sure.	Time reqd. to reach equilib. (min.)	Initial pres- sure (mm.)	Total fall in pres- sure (mm.)	% Re- duction in pres- sure.	Time reqd. to reach equilib. (min.)
1	4.8	191.0	28.0	14.6	105	188.0	28.5	15.1	150	201.0	30.5	15.1	90	196.0	28.0	14.3	90
2	6.0	257.0	35.0	13.6	165	261.0	36.5	13.9	135	276.5	42.5	15.4	105	261.5	40.5	15.5	75
3	7.2	323.0	44.0	13.6	120	322.5	41.0	12.7	135	333.0	50.5	15.1	120	320.0	47.5	14.9	105
4	8.25	383.5	40.5	10.5	120	394.0	48.5	12.3	120	405.0	57.5	13.6	90	420.0	65.0	15.2	90

In studying the influence of temperature it was not possible to take a constant pressure at different temperatures. The pressure varies between 188-201, 257-276.5, 320-333 and 383.5-420 mm.

TABLE II  
*Carbon monoxide + hydrogen : Influence of initial gas pressure and temperature.*

No.	Applied potential (kV).	30°				50°				70°			
		Initial pressure (mm.)	Total fall in pressure (mm.)	% Reduction in pressure.	Time reqd. to reach equilib. (min.)	Initial pressure (mm.)	Total fall in pressure (mm.)	% Reduction in pressure.	Time reqd. to reach equilib. (mm.)	Initial pressure (mm.)	Total fall in pressure (mm.)	% Reduction in pressure.	Time reqd. to reach equilib. (min.)
1	3.3	145	10.0	6.9	5	140	2.0	1.4	10	143	1.0	0.7	5
2	4.05	193	11.0	5.7	10	186	4.9	2.6	10	196	4.9	2.5	10
3	4.8	256	25.0	9.7	30	260	21.0	8.1	90	280	16.5	5.9	90
4	6.9	374	36.0	9.6	45	383	67.0	17.5	90	386	50.0	12.9	165
5	9.0	516	42.0	8.1	75								

In studying the influence of temperature it was not possible to take a constant pressure at different temperatures. The pressure varies between 140-145, 186-196, 256-280 and 374-386 mm.

TABLE III

*Velocity constant of CO-H<sub>2</sub> reaction in the initial stage of discharge.*

Temp.	Initial pressure (a)	Pressure after 2 min. (a-x)	Pressure after 5 min. (a-x')	Pressure after 10 min. (a-x'')	$k_{\text{(bimol.)}} = \frac{1}{a t} \times \frac{x}{(a-x)}$		
					$k_{\frac{1}{2} \text{ min.}} \times 10^{-4} \text{ min}^{-1}$	$k_{5 \text{ min.}} \times 10^{-4} \text{ min}^{-1}$	$k_{10 \text{ min.}} \times 10^{-4} \text{ min}^{-1}$
30°	145 mm.	140.8 mm.	135 mm.	135 mm.	10.28	10.22	—
"	193	188.8	183	182	5.762	5.661	3.131
"	256	248.9	239	235	5.572	5.556	3.490
"	374	361.5	344	342	4.623	4.662	2.501
"	516	484.0	479	475	6.407	2.994	1.673
50°	140	139.6	139	138	1.026	1.028	1.035
"	186	185.0	183.5	181.1	1.453	1.464	1.455
"	260	252.0	250	248	6.105	3.077	1.861
"	383	374.5	362.5	358	2.963	2.953	1.823
70°	143	142.6	142	142	0.981	0.985	—
"	196	195.0	193.5	191.1	1.308	1.318	1.308
"	280	276.0	273	270	2.588	2.007	1.322
"	386	376.0	371	369	3.445	2.094	1.193

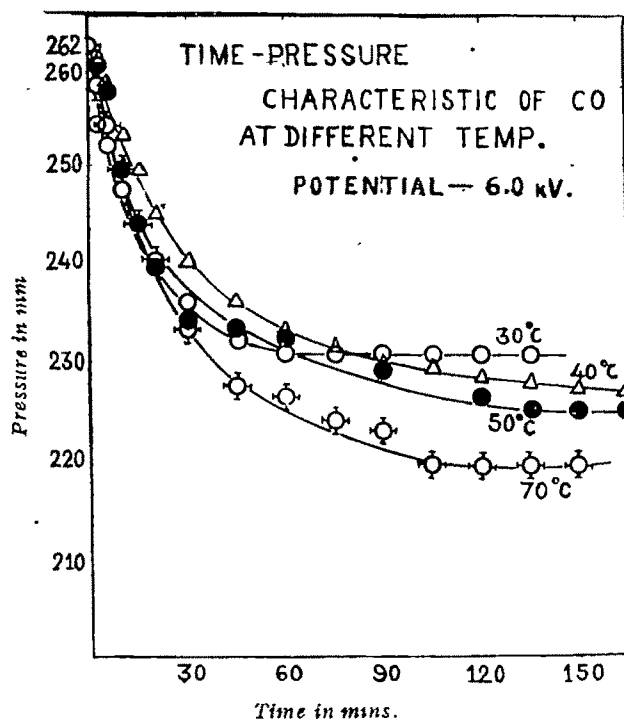
TABLE IV

*Velocity constants (near the equilibrium) of CO.*

Time (mins.)	70°		50°		40°	
	Initial pressure a=333 mm.	Initial pressure a=261 mm.	Initial pressure a=322.5 mm.	Initial pressure a=394 mm.	Initial pressure a=191 mm.	Initial pressure a=257 mm.
	$a-x$	$a-x$	$a-x$	$a-x$	$a-x$	$a-x$
	$k_{\text{unimol.}} \times 10^{-3} \text{ min}^{-1}$	$k_{\text{unimol.}} \times 10^{-3} \text{ min}^{-1}$	$k_{\text{unimol.}} \times 10^{-3} \text{ min}^{-1}$	$k_{\text{unimol.}} \times 10^{-3} \text{ min}^{-1}$	$k_{\text{unimol.}} \times 10^{-3} \text{ min}^{-1}$	$k_{\text{unimol.}} \times 10^{-3} \text{ min}^{-1}$
45	291.5	2.96	291.0	2.29	171.0	2.46
60	291.5	2.22	291.5	1.75	170.5	1.89
75	287.5	1.95	290.0	1.4	166.0	1.87
90	287.5	1.63	288.0	1.26	164.0	1.69
105	285.5	1.46	285.0	1.18	163.0	1.50
120	282.5	1.37	282.5	1.10		
135		224.5	281.5	1.01		
150						
165						

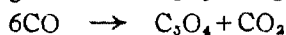
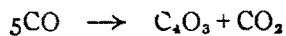
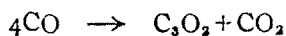
In the case of CO-H<sub>2</sub> mixture it is difficult to mark a sharp equilibrium point ; the change is rapid in the first few minutes and proceeds on more gradually over a long duration. The progress of the change with increasing temperature, however, unlike as in the case of CO, is markedly retarded (Table II, columns 3 and 2, Fig. 3).

Fig. 2



## DISCUSSION

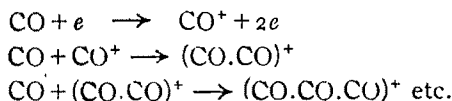
The pressure reduction (self condensation) of CO is well explained by the fact that carbon suboxides and CO<sub>2</sub> are formed according to a change along the following lines (Brodie, Berthelot, Ott, Crespi and Lunt, *loc. cit.*):



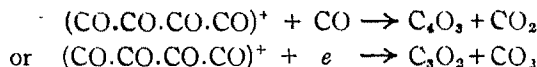
No data, excepting one by Lunt and Mumford (*J. Chem. Soc.*, 1929, 1711; cf. also *ibid.*, 1925, 2052) are available in the literature about the pressure variations by discharge in the above systems. The present work indicates a change which is never more than 17% reduction (vide Table I). From this it is clear that the above reaction(s) never proceeds to completion which would require a pressure change of 75% or more. It is suggested therefore that the reactions (decompositions) of CO are reversible. This view is supported by the fact that the steady state (equilibrium point) can be influenced by a change in temperature which probably alters the effective concentration of carbon suboxides (Table I, column 2).

The observation that the rate of reduction in pressure is rapid (vide Fig. 2) in the first few minutes, and later on slows down and tends towards uniformity suggests that the nature, and presumably, the order of the reaction in the first few minutes might be different from the one at the later stage. Carbon suboxides are the principal products of this reaction. They might arise in two ways: (1) by multiple collisions of CO molecules, and (2) by a stepwise building up from charged or excited CO molecules.

Since the probability of the former is very restricted in a gaseous system, the latter mechanism has been generally favoured (Lind, "The Chemical effects of alpha particles and electrons", The Chem. Catalog Co., New York, 1928; Mund, *Ann. Soc. Sci. Brux.*, 1931, B, 51, 1; 1934, 54, 30; Livingston, *Bull. Soc. Chim. Belg.*, 1936, 46, 334). When subjected to electrical field CO might give rise to positive ions by ionisation which in their turn might associate with other neutral or excited molecules giving rise to loose aggregations, called 'clusters' (Caress and Rideal, *loc. cit.*), e.g.



and so on, which on neutralisation of their charge or/and dissociation due to further electron impact yield various suboxides and  $\text{CO}_2$ :



The whole process may be akin to simple polymerisation, in this case brought about by electrical excitation of unsaturated CO molecules.

Thus, the reduction in pressure of CO may be attributed to two causes: (i) to a small extent due to the formation of slow moving ionic clusters, and (ii) largely because of the formation of solid carbon suboxides from the former. At higher gas pressures, because of the smaller mean free path, it may be expected that the rate of formation of these slow moving cluster ions would be more than the rate at which they dissociate into smaller fragments, viz. neutral oxides of carbon, with the result that the percentage fall in pressure would be less. A similar phenomenon has been observed by Holt (*J. Chem. Soc.*, 1909, 95, 30) in the case of dry  $\text{CO}_2$ .

A rise in temperature of the reaction vessel, according to general theories would bring about an augmented dissociation or/and decomposition of the cluster ions and consequent 'building-up' of high molecular weight structures, e.g., solids (*vide supra*). Therefore, it is to be anticipated that at higher temperature of CO, fall in pressure would be greater (Table I, columns 3 and 2) and the time required for reaching the equilibrium shorter (Table I, column 4).

It is difficult to assign quantitatively any mechanism, and therefore, the order to the reaction in the earlier stage. But the velocity constants,  $k$ , calculated according to the unimolecular expression reasonably point to the conclusion that in the later stages (near the equilibrium) it is unimolecular (Table IV). This probably suggests that it is only the transformation of carbon suboxides or clusters that predominates in the later stages. In the earlier stages the reaction cannot be represented as a simple mono- or bi-order process. This is to be expected on the mechanism suggested above.

Fig. 3

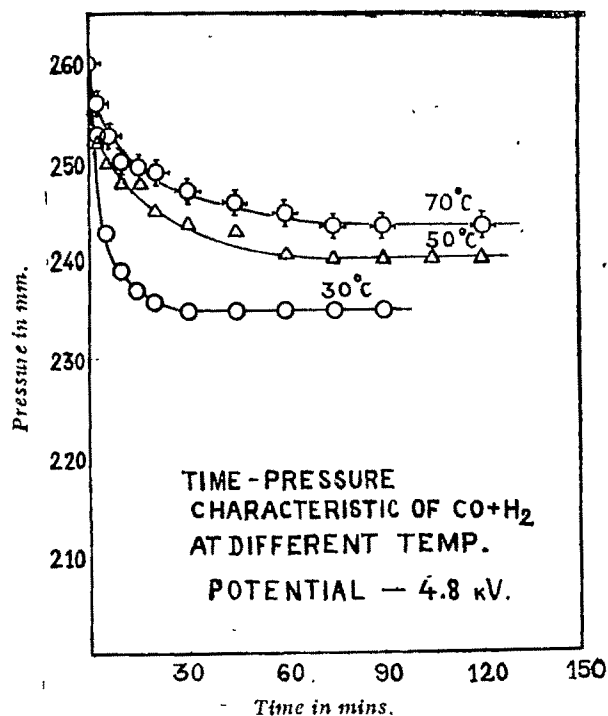
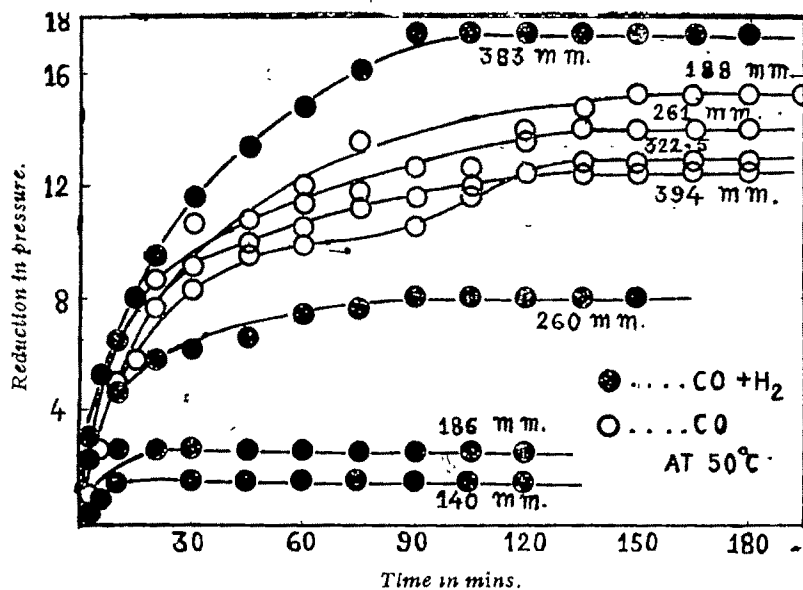


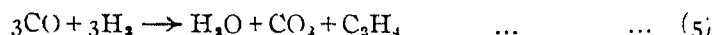
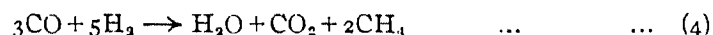
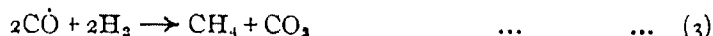
Fig. 4



A mixture of CO and H<sub>2</sub>, when subjected to silent electric discharge, is known to give a number of products viz. H.CHO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, CH<sub>2</sub>OH.CHO, C<sub>2</sub>H<sub>4</sub> etc.



The formation of these has been variously represented (Losanitsch, Löb, Wendt and Evans, Koenig and Wenig, *loc. cit.*):



As will be seen, excepting (1), all these changes are multi-order reactions and therefore have a very restricted possibility in a gaseous system.

The values of the velocity constant (vide Table III) calculated according to the bimolecular expression, show a remarkable constancy, except for one at a long exposure viz. 10 min, indicating that it is the change (1) which predominates. Work of the authors on the formation of H.CHO using large quantities of CO and H<sub>2</sub> also points to the same conclusion (unpublished data). Further it has also been shown that self-condensation of CO in presence of H<sub>2</sub> is not appreciable (Caress and Rideal, *loc. cit.* Sahasrabudhey and Deshpande, *Proc. Ind. Acad. Sci.*, 1950, **31A**, 322). The large fall in pressure in the earlier stages of discharge (vide Fig. 3) may thus be attributed to the primary reaction (1).

The lower values of fall in pressure at higher temperatures of the reaction vessel (Table II, columns 3 and 2) may be explained in view of the adverse influence of temperature on the exothermic reaction



and also partly on the depolymerising action of temperature on the formaldehyde polymers. Further work is in progress.

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CHEMISTRY DEPARTMENT,  
BANARAS HINDU UNIVERSITY.

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## STUDIES IN ELBS PERSULPHATE OXIDATION. PART I. OXIDATION OF SOME COUMARIN DERIVATIVES

BY R. J. PARIKH AND SURESH SETHNA

4-Methylcoumarin, 7-methoxy-4-methylcoumarin, 5-methoxy-4:7-dimethylcoumarin, 5:7-dimethoxy-4-methylcoumarin and 7:8-dimethoxy-4-methylcoumarin have been oxidised with potassium persulphate in alkaline solution and the corresponding 6-hydroxycoumarin derivatives are obtained in good yields. The methyl ethers have been demethylated and the hitherto unknown 5:6-dihydroxy-4:7-dimethyl-, 5:6:7-trihydroxy-4-methyl-, and 6:7:8-trihydroxy-4-methylcoumarins have been obtained. The completely methylated coumarins are dissolved by opening out the  $\alpha$ -pyrone ring by warming on a steam-bath and then oxidised with potassium persulphate. In actual practice therefore it is the *o*-hydroxycinnamic acid derivative which is oxidised in each case, the coumarin ring being formed again when the reaction mixture is acidified.

Elbs (*J. prakt. Chem.*, 1893, **48**, 179) oxidised *o*-nitrophenol to nitroquinol by the action of ammonium persulphate in presence of alkali. Later, potassium persulphate was substituted for ammonium persulphate and the reaction extended to other substituted phenols (D.R.P., 81,068; 81,297; 81,298. Chemische Fabrik Auf Aktienform. E. Schering. See Friedländer, "Fortschritte der Teerfarben Fabrikation", 1894-1897, Part IV, pp. 126, 127 and 121 respectively).

This reaction has been successfully applied by a number of workers to various derivatives of phenols like aldehydes, ketones and acids (Neubauer and Flatow, *Z. physiol. Chem.*, 1907, **52**, 375; Bargellini and Aureli, *Atti. R. Accad. Lincei*, 1911, **20**, 118; Bargellini, *Gazzetta*, 1915, **45**, 90; Hodgson and Beard, *J. Chem. Soc.*, 1927, 2339; Baker and co-workers, *ibid.*, 1938, 1602; 1939, 959, 1922; 1941, 667, 669; and others). Baker and Brown (*J. Chem. Soc.*, 1948, 2303) have worked out the general reaction conditions and have also suggested a mechanism for this reaction. Seshadri and his co-workers (*Proc. Ind. Acad. Sci.*, 1947, **28A**, 417, 427, 432, 444 *et seq.*) have in recent years successfully applied this method extensively to the flavones and synthesised a large number of natural flavones. The oxidation in all these cases is found to take place in the *para* position to the hydroxyl group if that position is free, and in the *ortho* position, if the *para* position is occupied. In the latter case the yields are very poor.

As a part of the systematic study of the reactivity of coumarin derivatives, which is being actively pursued in these laboratories, it was thought of interest to study systematically the application of this reaction to coumarin derivatives.

Only a few coumarins have been previously subjected to this reaction. Bargellini and Monti (*Gazzetta*, 1915; **45**, 90) oxidised coumarin and 7-methoxycoumarin. Wessely and Demmer (*Ber.*, 1929, **62**, 120) oxidised 7:8-dimethoxycoumarin and 7-methoxy-8-ethoxycoumarin, and Mauthner (*J. prakt. Chem.*, 1939, **162**, 23) oxidised 8-methoxycoumarin. In all the cases 6-hydroxycoumarin derivatives were obtained. The reaction has now been applied to a number of coumarin derivatives. Preliminary investigations

carried out with hydroxycoumarins showed that generally pasty uncrystallisable products were obtained and wherever a definite product could be isolated, the yield of the oxidation product was very poor. As the oxidation is carried out in alkaline medium the  $\alpha$ -pyrone ring is likely to open out and the additional hydroxy group, so formed, may not only help general oxidation, but it may also lead to a mixture of different products in oxidation. In view of this it was decided to first study the oxidation of completely methylated coumarin derivatives.

4-Methylcoumarin, 7-methoxy-4-methylcoumarin, 5-methoxy-4:7-dimethylcoumarin, 5:7-dimethoxy-4-methylcoumarin and 7:8-dimethoxy-4-methylcoumarin have been oxidised, the oxidation being carried out in all cases according to the general reaction method given by Baker and Brown (*loc.cit.*).

4-Methylcoumarin on oxidation gave the known 6-hydroxy-4-methylcoumarin as shown by direct comparison with an authentic specimen prepared by the Pechmann method. 7-Methoxy-4-methylcoumarin gave 6-hydroxy-7-methoxy-4-methylcoumarin which on demethylation with hydriodic acid gave the known 6:7-dihydroxy-4-methylcoumarin which was also obtained in a very poor yield by the oxidation of 7-hydroxy-4-methylcoumarin. That the oxidation has taken place in the 6 position is shown by the fact that the dihydroxy compound obtained on demethylation has m.p.  $275^{\circ}$ , identical with the known 6:7-dihydroxy-4-methylcoumarin (Appel, *J. Chem. Soc.*, 1935, 1031). The isomeric 7:8-dihydroxy-4-methylcoumarin has m.p.  $235^{\circ}$  (Pechmann and Duisberg, *Ber.*, 1883, 16, 2122); Bargellini and Martegiani (*Gazzetta*, 1911, 41, 612) obtained on methylation of 6:7-dihydroxy-4-methylcoumarin, the dimethyl ether (m.p.  $130-34^{\circ}$ ) and a monomethyl ether (m.p.  $173-75^{\circ}$ ) to which the constitution was not assigned. As 6-hydroxy-7-methoxy-4-methylcoumarin obtained in this work has m.p.  $209^{\circ}$ , the monomethyl ether of Bargellini and Martegiani is very likely 6-methoxy-7-hydroxy-4-methylcoumarin. Baker and Evans (*J. Chem. Soc.*, 1938, 374), however, give m.p.  $213^{\circ}$  for this compound. 5-Methoxy-4:7-dimethylcoumarin, 7:8-dimethoxy-4-methylcoumarin and 5:7-dimethoxy-4-methylcoumarin on oxidation gave products to which the structures of 5-methoxy-6-hydroxy-4:7-dimethylcoumarin, 7:8-dimethoxy-6-hydroxy-4-methylcoumarin and 5:7-dimethoxy-6-hydroxy-4-methylcoumarin respectively have been assigned by analogy with the previous work. All these coumarin derivatives are found to give a deep yellow solution with caustic alkalis as given by the known 6-hydroxycoumarin derivatives. The methoxycoumarins have been demethylated with hydriodic acid and the hitherto unknown 5:6-dihydroxy-4:7-dimethyl-, 6:7:8-trihydroxy-4-methyl-, and 5:6:7-trihydroxy-4-methylcoumarins have been obtained. In the case of 5-hydroxycoumarins the hydroxy compounds were again methylated and compared with the completely methylated coumarins and were found to be the same. This was done in order to find out if the ring had opened out and closed again in the other direction, as it sometimes happens in the case of flavones.

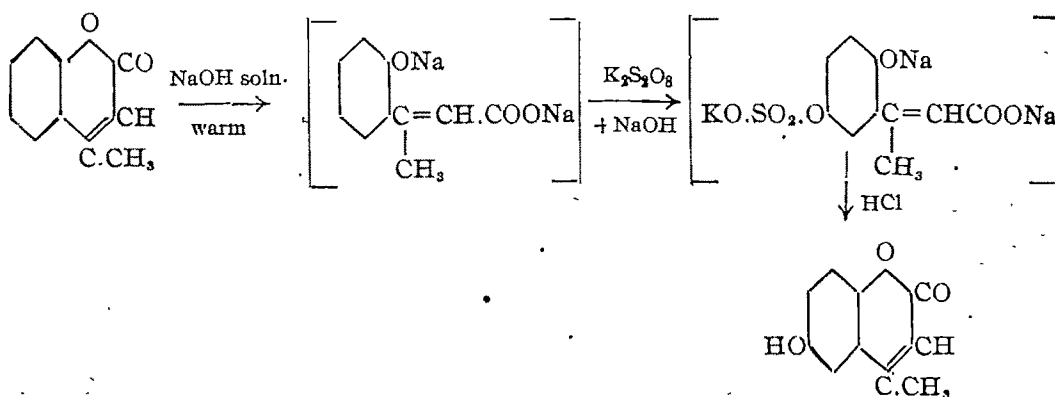
The completely methylated coumarins are naturally not soluble in cold alkali and the reaction does not proceed when they are merely suspended in alkali. It has been found that if the methoxycoumarins are warmed on a steam-bath with 10% alkali for some time, they go into solution, presumably because the  $\alpha$ -pyrone ring opens out and an *o*-hydroxycinnamic acid derivative is formed. The position *para* to the hydroxy group

formed by the opening of the ring is the 6 position in the original coumarin and therefore oxidation takes place in this position. In actual practice therefore, it is the *o*-hydroxycinnamic acid derivative which is oxidised, the coumarin ring being formed again when the reaction mixture is acidified. The successful oxidation of the coumarin derivatives therefore depends on this technique of opening out the  $\alpha$ -pyrone ring of the methoxycoumarin derivatives. The following table gives the yields of the oxidation products.

TABLE I

	Starting material recovered.	Yield of the oxidation product. % of the theoretical	
		on the basis of the starting material.	allowing for the recovery.
1. 4-Methyl-	25%	41.7	45.4
2. 7-Methoxy-4-methyl-	31.3	17.3	25.2
3. 5-Methoxy-4:7-dimethyl-,	12.1	40	53.9
4. 5:7-Dimethoxy-4-methyl-	25	24.7	33.6
5. 7:8-Dimethoxy-4-methyl-	20.5	25.4	32

The work is being extended to the synthesis of several unknown and natural coumarins.



#### EXPERIMENTAL

*Oxidation of 4-Methylcoumarin : 6-Hydroxy-4-methylcoumarin.*—4-Methylcoumarin (2.4 g.), prepared according to Woodruff ("Organic Synthesis", Vol. 24, p. 69) was dissolved in sodium hydroxide (3 g. in 30 c.c. water) by heating on a steam-bath. The solution was then cooled and potassium persulphate (4.5 g. in 100 c.c.) was added gradually from a separating funnel during 3 hours. The solution was mechanically stirred and the temperature was not allowed to rise above 10°. After the addition was complete the reaction mixture was stirred for half an hour more and left overnight. Next day it was just acidified with concentrated hydrochloric acid when some product (0.4 g.)

separated which was found to be the original coumarin. The filtrate was extracted with ether when a further quantity (0.2 g.) of the original coumarin was obtained. To the aqueous layer more hydrochloric acid (conc., 50 c.c.) was added and the solution heated on a steam-bath for 40 minutes. The solution was cooled and the product which separated out was filtered and crystallised from rectified spirit in plates (0.9 g.), m.p. 242°. Mixed m.p. with an authentic specimen of 6-hydroxy-4-methylcoumarin, prepared by the Pechmann method from quinol (Borsche, *Ber.*, 1907, **40**, 2732), was not depressed. The filtrate was extracted with ether and the ethereal layer gave a further quantity (0.2 g.) of the oxidised product. The oxidation product dissolved in sodium hydroxide to give a deep yellow solution.

*Oxidation of 7-Methoxy-4-methylcoumarin*: 6-Hydroxy-7-methoxy-4-methylcoumarin.—7-Hydroxy-4-methylcoumarin (Pechmann and Duisberg, *Ber.*, 1883, **16**, 2122) was methylated according to Limaye and Bhide (*Rasayanam*, 1938, 138). 7-Methoxy-4-methylcoumarin (6.4 g.) was dissolved in sodium hydroxide (7 g. in 70 c.c. of water) by heating on a steam-bath and oxidised with potassium persulphate (9.9 g. in 200 c.c. of water). The reaction mixture was worked up as before. The product (2 g.) which came down on just acidifying the solution was found to be the original coumarin. The product which was obtained after heating with excess of hydrochloric acid (conc., 150 c.c.) was crystallised from dilute alcohol in needles (1.2 g.), m.p. 208-209°. (Found: C, 64.3; H, 4.7.  $C_{11}H_{10}O_4$  requires C, 64.1; H, 4.9 per cent). The substance dissolves in sodium hydroxide to give a deep yellow solution.

6:7-Dimethoxy-4-methylcoumarin.—The above coumarin (0.5 g.) was dissolved in dry acetone (50 c.c.) and refluxed for 20 hours with methyl iodide (3 c.c.) and anhydrous potassium carbonate (1 g.). The reaction mixture was then filtered and the product obtained on removal of acetone was crystallised from very dilute alcohol in needles (0.3 g.), m.p. 133-34°. (Found: C, 65.5; H, 5.0. Calc. for  $C_{12}H_{12}O_4$ : C, 65.5; H, 5.5 per cent). Bargellini and Martegiani (*loc. cit.*) give m.p. 130-34°.

6:7-Dihydroxy-4-methylcoumarin.—6-Hydroxy-7-methoxy-4-methylcoumarin (0.5 g.) was heated with acetic anhydride (5 c.c.) and hydriodic acid (d 1.7, 5 c.c.) in an oil-bath at 130°-140° for 2 hours and the reaction mixture poured in cold sodium bisulphite solution. The product obtained was crystallised from rectified spirit in needles (0.3 g.), m.p. 275°. (Found: C, 62.4; H, 4.2. Calc. for  $C_{10}H_8O_4$ : C, 62.5; H, 4.1 per cent). Appel (*loc. cit.*) gives the same m.p. Bargellini and Martegiani (*loc. cit.*) give m.p. 269°. The product dissolves in sodium hydroxide to give an orange solution and it gives a green colour with alcoholic ferric chloride. This coumarin was also obtained in a very poor yield by the oxidation of 7-hydroxy-4-methylcoumarin (4.4 g.) in sodium hydroxide (5 g. in 50 c.c. of water) solution with potassium persulphate (7 g. in 150 c.c. of water) and working up the reaction mixture as usual.

*Oxidation of 5-Methoxy-4:7-dimethylcoumarin*: 6-Hydroxy-5-methoxy-4:7-dimethylcoumarin.—5-Hydroxy-4:7-dimethylcoumarin (Pechmann and Cohen, *Ber.*, 1884, **17**, 2187) (6 g.) was methylated in acetone solution with methyl iodide (10 c.c.) in presence of potassium carbonate as usual by refluxing for 20 hours, m.p. 147°, yield 5.8 g. Collie and Chrystall (*J. Chem. Soc.*, 1907, **91** 1805) give m.p. 146°.

5-Methoxy-4:7-dimethylcoumarin (5 g.) was dissolved in sodium hydroxide (5 g. in 50 c.c. of water) solution by warming on a steam-bath and oxidised as before with potassium persulphate (7.4 g. in 160 c.c. of water). On working up the reaction mixture the product, which came down on just acidification of the mixture, was found to be the starting material (0.7 g.). The product obtained on heating with excess of hydrochloric acid (conc., 150 c.c.) was crystallised from rectified spirit in tiny needles (2.5 g.), m.p. 175°. (Found: C, 65.0; H, 5.5.  $C_{12}H_{12}O_4$  requires C, 65.5; H, 5.5 per cent). It dissolves in alkali to give a deep yellow solution.

5:6-Dimethoxy-4:7-dimethylcoumarin.—The above coumarin (0.5 g.) was dissolved in acetone and refluxed for 24 hours with methyl iodide (3 c.c.) and anhydrous potassium carbonate (2 g.). The product obtained on working up the reaction mixture as before was crystallised from methyl alcohol in plates (0.3 g.), m.p. 96°. (Found: C, 66.5; H, 5.8.  $C_{13}H_{14}O_4$  requires C, 66.7; H, 6.0 per cent).

5:6-Dihydroxy-4:7-dimethylcoumarin.—6-Hydroxy-5-methoxy-4:7-dimethylcoumarin (0.6 g.) was dissolved in acetic anhydride (5 c.c.) and hydriodic acid (*d* 1.7, 5 c.c.) was added. The reaction mixture was heated in an oil-bath between 135° and 140° for 2 hours. The product, obtained on pouring the reaction mixture in sodium bisulphite solution, was crystallised from rectified spirit in tiny needles (0.4 g.), m.p. 260°. (Found: C, 63.8; H, 4.4.  $C_{11}H_{10}O_4$  requires C, 64.1; H, 4.9 per cent). It gives a deep red solution with alkali and a brownish coloration with alcoholic ferric chloride. This hydroxy-coumarin was methylated again by the methyl iodide-potassium carbonate method when 5:6-dimethoxy-4:7-dimethylcoumarin was obtained, as seen by direct comparison.

Oxidation of 5:7-Dimethoxy-4-methylcoumarin: 6-Hydroxy-5:7-dimethoxy-4-methylcoumarin.—5:7-Dihydroxy-4-methylcoumarin (Pechmann and Cohen, *loc. cit.*) was methylated with dimethyl sulphate and alkali (Head and Robertson, *J. Chem. Soc.*, 1931, 1258). The dimethoxycoumarin (10 g.) was dissolved in sodium hydroxide (9 g. in 90 c.c. of water) by heating on a steam-bath and oxidised with potassium persulphate (13 g. in 260 c.c. of water) as before. The product (2.5 g.) which came down on just acidification was found to be the starting material. The product, obtained on heating with excess of hydrochloric acid (conc., 200 c.c.), was crystallised from dilute alcohol in square plates (2.65 g.), m.p. 195°. (Found: C, 61.3; H, 5.0.  $C_{12}H_{12}O_5$  requires C, 61.0; H, 5.1 per cent). It dissolves in alkali to give a deep yellow solution.

5:6:7-Trimethoxy-4-methylcoumarin was prepared from the above coumarin (0.8 g.), methyl iodide (5 c.c.) and anhydrous potassium carbonate (1.5 g.) as usual and was crystallised from dilute alcohol in thin plates (0.6 g.), m.p. 115–16°. (Found: C, 62.5; H, 5.3.  $C_{13}H_{14}O_5$  requires C, 62.4; H, 5.6 per cent).

5:6:7-Trihydroxy-4-methylcoumarin.—6-Hydroxy-5:7-dimethoxy-4-methylcoumarin (0.5 g.) was heated with acetic anhydride (5 c.c.) and hydriodic acid (*d* 1.7, 4 c.c.) at 135°–140° for 3 hours. The product, obtained on pouring the reaction mixture in sodium bisulphite solution, was crystallised from rectified spirit in needles (0.3 g.), m.p. 278°. (Found: C, 57.8; H, 3.9.  $C_{10}H_8O_5$  requires C, 57.6; H, 3.8 per cent). It dissolves in alkali to give a brown solution with intense green fluorescence and gives a violet colour with alcoholic ferric chloride.

This hydroxycoumarin was methylated again by the methyl iodide-potassium carbonate method when 5:6:7-trimethoxy-4-methylcoumarin was obtained, as seen by direct comparison.

*Oxidation of 7:8-Dimethoxy-4-methylcoumarin: 6-Hydroxy-7:8-dimethoxy-4-methylcoumarin.*—7:8-Dihydroxy-4-methylcoumarin (Pechmann and Duisberg, *loc. cit.*) was methylated by the methyl iodide-potassium carbonate method and the dimethyl ether, m.p.  $135^{\circ}$ , was obtained. Sakai and Chotar (*J. Pharm. Soc. Japan*, 1935, **55**, 691; *Chem. Abs.*, 1935, **29**, 7311) give m.p.  $132^{\circ}$ .

The dimethoxycoumarin (4.4 g.) was dissolved in sodium hydroxide (4.0 g. in 40 c.c. of water) by warming and oxidised as before with potassium persulphate (5.9 g. in 125 c.c. of water). On working up the reaction mixture as before 0.9 g. of the original product was recovered. The oxidation product obtained was crystallised from alcohol in needles (1.2 g.), m.p.  $179^{\circ}$ . (Found: C, 60.9; H, 4.6.  $C_{12}H_{12}O_6$  requires C, 61.0; H, 5.1 per cent). It dissolves in alkali to give a deep yellow solution.

*6:7:8-Trimethoxy-4-methylcoumarin.*—The above coumarin (0.5 g.) was methylated with methyl iodide (3 c.c.) and potassium carbonate (1 g.) in acetone solution as usual and the product obtained was crystallised from dilute alcohol in square plates (0.35 g.), m.p.  $113^{\circ}$ . (Found: C, 61.8; H, 5.2.  $C_{15}H_{14}O_6$  requires C, 62.4; H, 5.6 per cent).

*6:7:8-Trihydroxy-4-methylcoumarin.*—6-Hydroxy-7:8-dimethoxy-4-methylcoumarin (0.7 g.) was heated with acetic anhydride (5 c.c.) and hydriodic (d 1.7, 5 c.c.) in an oil-bath at  $135^{\circ}$ - $140^{\circ}$  for 2 hours. The product obtained on working up as usual was crystallised from rectified spirit in needles (0.5 g.), m.p.  $274$ - $76^{\circ}$ . (Found: C, 53.3; H, 4.3.  $C_{10}H_8O_6$ , 1  $H_2O$  requires C, 53.1; H, 4.4 per cent). It dissolves in alkali to give a deep orange solution and gives a deep blue coloration with alcoholic ferric chloride.

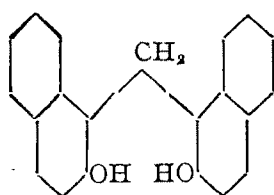
The thanks of the authors are due to Dr. R.C. Shah for his kind interest in the work.

# STUDIES ON THE REDUCTION OF DEHYDRODI-2-HYDROXY-1-NAPHTHYLMETHANE AND ITS DERIVATIVES

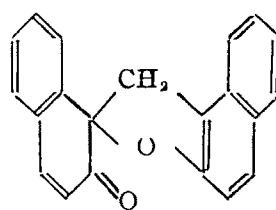
By J. N. CHATTERJEA

The catalytic reduction of dehydrodi-2-hydroxy-1-naphthylmethane and its derivatives have been studied.

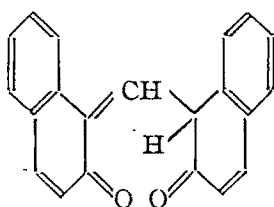
Dehydrodi-2-hydroxy-1-naphthylmethane, obtained by the mild alkaline oxidation of di-2-hydroxy-1-naphthylmethane (I) (Abel, *Ber.*, 1892, **25**, 3477) was given the structure (II) by Pummerei and Cherbuliez (*Ber.*, 1914, **47**, 2957) who showed that it gave a monophenyldiazone and recognised its analogy with bimolecular dehydrophenols. A second structure (III) proposed by Kohn and Osterseizer (*Monatsh.*, 1918, **39**, 299) and



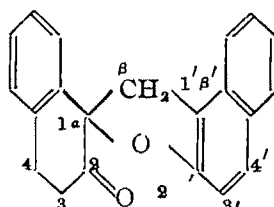
(I)



(II)



(III)



(IV)

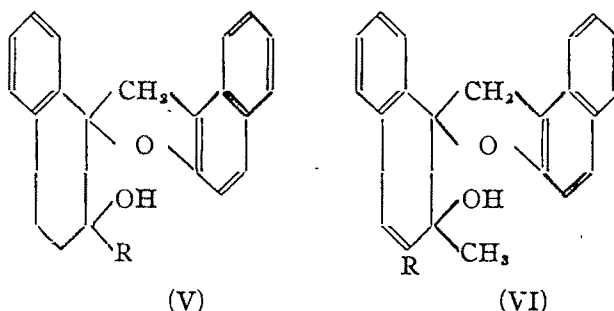
advocated by Dischendorfer (*Ber.*, 1926, **59**, 774; *Monatsh.*, 1927, **48**, 543) was rejected by Shearing and Smiles (*J. Chem. Soc.*, 1937, 1931) who supported the structure (II) and pointed out the inadequacy of the structure (III) in the light of the behaviour of the compound and the mechanism of its formation.

The significant characteristics of the structure (II) are the 1:2'-oxide linkage and the  $\alpha$ : $\beta$ -unsaturated ketone system. The presence of a double bond at 3:4 position was shown by Shearing and Smiles (*loc. cit.*) by the preparation of a dibromide which on treatment with pyridine loses hydrogen bromide giving 3-bromodehydrodi-2-hydroxy-1-naphthylmethane. More evidence of the correctness of the structure (II) has been obtained from a study of the behaviour of the compound and its derivatives towards catalytic hydrogenation.

Whilst reduction of the dehydromethane by zinc dust and acetic acid leads to the rupture of the 1:2'-oxide linkage giving (I) (Abel, *loc. cit.*), it has now been found that



catalytic hydrogenation in the presence of a mild catalyst, such as palladised barium sulphate (Pd, 5%), gives in addition the ketone (IV), characterised by the preparation of a semicarbazone. Hydrogenation with a more active catalyst, such as palladised charcoal (Pd, 30%), gave (I) as the main product together with a secondary alcohol (V, R=H), characterised as its benzoyl derivative. A poorer yield of (V, R=H) was obtained when Adams's catalyst was employed, the main product being again (I). The analogous catalytic reduction of 3-bromodehydrodi-2-hydroxy-1-naphthylmethane with a variety of catalysts led to the exclusive rupture of the oxide linkage giving 3-bromodi-2-hydroxy-1-naphthylmethane.



Catalytic hydrogenation was next tried on (VI, R=H), prepared by Kohn and Ostersetzer (*loc. cit.*) by the action of methylmagnesium iodide on the dehydromethane. Whilst the compound is unaffected by zinc and acetic acid (Shearing and Smiles, (*loc. cit.*)), it has now been observed that catalytic hydrogenation leads to the quantitative reduction of the isolated double bond giving (V, R=CH<sub>3</sub>) leaving the oxide link intact. Analogous reduction of (VI, R=Br) in the presence of Adams's catalyst gave the same product (V, R=CH<sub>3</sub>) by the loss of the bromine atom as hydrogen bromide. The reduction of (VI, R=H) with hydriodic acid and red phosphorus in acetic acid proved very interesting as the molecule was cleaved with the formation of 1:2-dimethylnaphthalene (identified as its picrate) in poor yield.

## E X P E R I M E N T A L

### *Catalytic Reduction of Dehydrodi-2-hydroxy-1-naphthylmethane*

(a) *With Palladised Barium Sulphate: Formation of spiro-(1:α)-2-ketotetralin-α':β'-(2':1')-naphthodihydrofurane (IV).*—Dehydrodi-2-hydroxy-1-naphthylmethane (0.5 g.) in ethyl acetate (50 c.c.) was hydrogenated at room temperature and ordinary pressure in the presence of palladised barium sulphate (5% Pd, 3 g.). Hydrogenation was complete with the absorption of one molecular proportion of hydrogen. The solution was then filtered and the solvent removed in vacuum. The residue was dissolved in ether and freed from phenolic impurities by washing with 2% sodium hydroxide. Evaporation of the dried ethereal solution left (IV) as a gum which could not be crystallised. The semicarbazone, obtained by treating the gum with semicarbazide hydrochloride (0.5 g.) and excess of sodium acetate in alcohol on the water-bath, crystallised from butanol in colorless prisms (0.15 g.), m.p. 215–16° (decomp.). For analysis a sample was dried at 100°/15 mm.,

over phosphorus pentoxide. (Found: C, 73.7; H, 5.3; N, 11.3.  $C_{22}H_{11}O_2N_3$  requires C, 73.9; H, 5.3; N, 11.9 per cent).

(b) *With Palladised Charcoal: Formation of spiro-(1: $\alpha$ )-2-hydroxytetralin- $\alpha'$ : $\beta'$ -(2':1')-naphthodihydrofurane (V, R=H).*—A suspension of dehydrodi-2-hydroxy-1-naphthylmethane (1.0 g.) in ethyl acetate (40 c.c.) was hydrogenated under similar conditions as in (a) above, in the presence of palladised charcoal (30% Pd, 0.2 g.). When the absorption was complete (1.3 molecular proportion), the solution was filtered and the solvent removed in vacuum. The neutral product (V, R=H) (0.2 g.) solidified in the presence of dilute alcohol and was obtained after two crystallisations from alcohol in colorless plates, m.p. 143–45°. (Found: C, 83.3; H, 5.9.  $C_{21}H_{18}O_2$  requires C, 83.4; H, 5.9 per cent). It dissolved in concentrated sulphuric acid with a yellow colour exhibiting intense green fluorescence. The benzoyl derivative was prepared by adding benzoyl chloride (0.2 g.) to a solution of the product (0.2 g.) in pyridine (2 c.c.) and leaving the mixture overnight. It crystallised from alcohol in colorless, hard prisms, m.p. 137–38°. (Found: C, 82.7; H, 5.4.  $C_{28}H_{22}O_3$  requires C, 82.7; H, 5.4 per cent).

(c) *With Adams's Catalyst.*—A suspension of dehydrodi-2-hydroxy-1-naphthylmethane (2.0 g.) in alcohol (50 c.c.) was hydrogenated under similar conditions in the presence of Adams's catalyst (0.1 g.). The absorption of hydrogen was complete in  $\frac{1}{2}$  hour (1.1 molecular proportion) and the mixture when worked up gave (V, R=H) (50 mg.) and (I) (1.6 g.).

*Catalytic Reduction of 3-Bromodehydrodi-2-hydroxy-1-naphthylmethane.*—A solution of 3-bromodehydrodi-2-hydroxy-1-naphthylmethane (1.0 g.) (Shearing and Smiles, *loc. cit.*) in ethyl acetate (50 c.c.) was hydrogenated at room temperature and ordinary pressure in the presence of palladised charcoal (30% Pd, 0.2 g.). The hydrogenation was complete in an hour (1 molecular proportion) and the product when worked up gave the alkali-soluble 3-bromodi-2-hydroxy-1-naphthylmethane (0.8 g.) crystallising from alcohol in colorless, felted needles, m.p. 202–204° (decomp.); Shearing and Smiles (*loc. cit.*) give m.p. 201°. (Found: C, 66.5; H, 3.8.  $C_{21}H_{18}O_2Br$  requires C, 66.5; H, 3.9 per cent). No neutral product was detected in this reduction.

*Catalytic Reduction of (VI, R=H): Formation of spiro-(1: $\alpha$ )-2-methyl-2-hydroxytetralin- $\alpha'$ : $\beta'$ -(2':1')-naphthodihydrofurane.*—The compound (VI, R=H) (1.0 g.) was dissolved in pure alcohol (50 c.c.) and hydrogenated under ordinary conditions in the presence of Adams's catalyst (0.1 g.). After 45 minutes, one mol. of hydrogen had been absorbed, and then the solution was filtered and concentrated when (V, R=CH<sub>3</sub>, 0.9 g.) was obtained in colorless needles, m.p. 163–64°. (Found: C, 83.7; H, 6.4.  $C_{22}H_{20}O_2$  requires C, 83.6; H, 6.3 per cent). The product is insoluble in alkali.

*Reduction of (VI, R=H) with Hydriodic Acid and Red Phosphorus.*—A solution of the compound (VI, R=H, 5.0 g.) in acetic acid was refluxed with hydriodic acid (d 1.7, 30 c.c.) and red phosphorus (5.0 g.) for  $\frac{1}{2}$  hour. The mixture was filtered, washed with acetic acid and the filtrate extracted with ether. The ethereal solution was washed with sodium bicarbonate and then with alkali. The alkaline extract on acidification gave a semi-solid product having the odour of  $\beta$ -naphthol, the presence of which was detected by diazo-couplings. The neutral product after the removal

of ether was purified by steam-distillation. The oily distillate was taken up with ether and distilled fractionally. The fraction distilling at  $260^{\circ}$ - $270^{\circ}$  was converted into the picrate, crystallising from alcohol in orange needles, m.p.  $125^{\circ}$ , undepressed on admixture with the picrate of 1:2-dimethylnaphthalene, m.p.  $130^{\circ}$ . (Found: C, 55.4; H, 3.7; N, 11.1.  $C_{18}H_{18}O_7N_3$  requires C, 56.1; H, 3.9; N, 10.9 per cent).

*Preparation of (VI, R=Br).*—A solution of methylmagnesium iodide (1.5 g.) and magnesium (0.25 g.) in ether was added dropwise to a stirred solution of 3-bromodehydrodi-2-hydroxy-1-naphthylmethane (3.0 g.) in benzene (40 c.c.). During the addition of the first few drops, the yellow colour of the solution seemed to deepen but immediately afterwards the colour began to fade away. The addition of the Grignard reagent was stopped when the solution became nearly colorless and after leaving at the ordinary temperature for  $\frac{1}{2}$  hour, the product, when worked up in the usual way, gave a gum which crystallised slowly when left in contact with alcohol for sometime. It crystallised from aqueous alcohol in colorless, hard prisms (2.5 g.), m.p.  $136$ - $137^{\circ}$ . (Found: C, 67.1; H, 4.5.  $C_{22}H_{17}O_2Br$  requires C, 67.2; H, 4.3 per cent). The product is insoluble in alkali.

*Catalytic Reduction of (VI, R=Br).*—A solution of the bromo compound (VI, R=Br, 0.5 g.) in alcohol (30 c.c.) was hydrogenated in presence of Adams's catalyst (50 mg.). Approximately 1.8 molecular proportion of hydrogen was absorbed, the absorption towards the end being very sluggish (apparently due to the poisoning of the catalyst). The product, which was insoluble in alkali, crystallised from alcohol in colorless, felted needles, m.p.  $159$ - $162^{\circ}$ , and was identical with (V, R=CH<sub>3</sub>) by comparison and mixed m.p. (Found: C, 83.5; H, 6.3.  $C_{22}H_{20}O_2$  requires C, 83.6; H, 6.3 per cent). The product also gave negative Beilstein's test for halogen.

The author wishes to thank Prof. Sir Robert Robinson, P. R. S., for his interest in the investigation.

DYSON PERRINS LABORATORY,  
OXFORD, ENGLAND.

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## ESSENTIAL OIL FROM THE BERRIES OF *LAVUNGO SCANDENS* (ROXB.)

By K. K. BASLAS AND S. S. DESHPANDE

The essential oil from the berries of *Lavungo Scandens* consists of 56% cineol, 30% cinnamyl cinnamate and 9% methyl cinnamate.

The plant *Lavungo Scandens* (Roxb.) Buch.-Ham exwight., known in Sanskrit as "*Lavang lala*" is indigenous to India and belongs to the family of Rutaceae. It is a stout scandent shrub of E. Bengal and Assam bearing white, very fragrant flowers, 1" in diameter and oblong berries with aromatic pulp. Neither the flowers nor the berries have been chemically examined for their aromatic constituents though the berries have been used for perfuming hair oils. They are said to be of high medicinal value, specially in curing baldness. On account of the extreme aroma they possess, they are commonly known as 'Sugandh kokila.'

The essential oil is obtained by the steam distillation of the dried berries in 2.5% yield. It has the following properties:  $d_{25}^{20}$ , 0.945;  $n_D^{25}$ , 1.5120;  $[\alpha]_D^{25}$ ,  $-1^\circ$ ; acid value, 1.93 and ester value, 102.5.

The oil (80 c.c.) was distilled at atmospheric pressure and the following fractions were collected:

- (I)  $176^\circ-178^\circ$ , 45 c.c.
- (II)  $243^\circ-245^\circ$ , 25 c.c.
- (III)  $261^\circ-263^\circ$ , 7 c.c.

Fraction (I) is strongly odorous and smells like camphor. It absorbs bromine and does not show any reducing properties, nor does it show the presence of any functional groups. Its boiling point and odour suggest its identity with cineol which has subsequently been confirmed. Thus, it forms a solid compound with syrupy phosphoric acid (Kebler, *Amer. J. Pharm.*, 1898, **70**, 492), and a crystalline compound with resorcinol melting at  $85^\circ-87^\circ$  (Baeyer and Virck, *Ber.*, 1902, **35**, 1209). The identity of this fraction with cineol was finally confirmed by preparing resorcinol addition compound with a genuine sample of cineol obtained by us from eucalyptus oil and observing the mixed melting point of the addition products, when no depression in the melting point was observed. Amount of cineol in the oil was estimated by treating it with a 50% solution of resorcinol and decomposing the solid addition compound obtained with caustic soda, when the cineol was liberated. Estimated in this way the percentage of cineol in the oil was found to be 56%.

Fraction (II) on redistillation boils at  $245^\circ$  and possesses a fine pleasant fruity odour. On keeping in ice, it freezes to a white creamy solid which melts at room

temperature. It shows indifference towards reagents for alcohols, aldehydes and ketones. When heated with Fehling's solution, the latter is not reduced, but a crystalline precipitate separates which has been proved to be sodium cinnamate. The fraction was hydrolysed with alkali and the acid and alcohol separated. The acid was identified as cinnamic acid from (a) its melting point, (b) its reaction with bromine and (c) its neutral equivalent. The alcohol was identified as cinnamyl alcohol from its boiling point, and the melting point of its dibromo derivative,  $74^{\circ}$  (Grimaux, *Ber.*, 1887, 20, 120). The ester is therefore cinnamyl cinnamate. This was further confirmed by preparing the dibromide of the ester which melted on recrystallisation at  $151^{\circ}$  (Gildmeister and Hoffman, "The Ethereal Oils," Vol. I, p. 646). The identity of the cinnamyl alcohol in the hydrolysis product of the ester was further confirmed by taking the mixed melting point of the bromo derivative obtained from the above alcohol and the bromo derivative prepared by us from a genuine sample of cinnamyl alcohol, when no depression was observed.

Fraction (III) boils at  $263^{\circ}$  and possesses a pleasant fruity odour like fraction (II). It also freezes on being kept in ice and melts to a liquid at room temperature. It also behaves similarly with Fehling's solution. On hydrolysis with alkali it forms a clear solution in water indicating that this fraction is an ester of cinnamic acid with some alcohol which is soluble in water. Among the naturally occurring esters of cinnamic acid, the possibility of methyl cinnamate suggests itself. This boils at  $263^{\circ}$  and freezes at  $33^{\circ}$ . The alcohol formed on hydrolysis of fraction (III) could not be isolated on account of its solubility in alcohol. The identity of methyl cinnamate in this fraction was confirmed by preparing the bromo derivative which melted after recrystallisation at  $117^{\circ}$ . It was further confirmed by taking the mixed melting point of the two bromo derivatives, one obtained from the ester present in fraction (III) and the other, prepared from a genuine sample of methyl cinnamate. No depression was observed in the melting point.

#### EXPERIMENTAL

*Isolation of the Essential Oil.*—The essential oil was obtained by steam distillation of the berries from a copper still fitted with a spiral copper condenser. The oil separated from the aqueous distillate as a light yellow layer floating over water. It was separated from water, dried over anhydrous sodium sulphate and distilled. It gave the properties as shown above.

TABLE I

Fraction No.	Boiling range.	Vol.	Yield.	Properties.
I.	$176^{\circ}$ - $178^{\circ}$	45 c.c.	56%	Addition product with phosphoric acid and also with resorcinol, m.p. $85^{\circ}$ - $87^{\circ}$ .
II.	$243^{\circ}$ - $245^{\circ}$	25	30	Dibromo addition product, m.p. $151^{\circ}$ . Freezes to a creamy solid on cooling.
III.	$261^{\circ}$ - $263^{\circ}$	7	9	Solidifies on cooling to a white creamy solid, bromo-derivative, m.p. $117^{\circ}$ .
Loss		3		

*Fractionation of the Oil.*—The oil (80 c.c.) on distillation at atmospheric pressure gave the following fractions, whose boiling points, boiling ranges, percentage yields and properties are shown in Table I.

*Identification of Cineol in Fraction (I): Addition Compound with Phosphoric Acid.*—The fraction (5 c.c.) was cooled in ice and salt and syrupy phosphoric acid (2 c.c., d 1.75) was gradually added with constant stirring. The solid addition compound separated and became harder on further cooling.

*Cineol-resorcinol Addition Compound.*—To the fraction (5 c.c.) was added resorcinol (1 g.) and the mixture warmed until resorcinol went into solution. On cooling, addition product separated in rhombic plates. On filtering, washing a little with alcohol, and drying the compound it melted at 80-85°. On recrystallisation its melting point rose to 85-87°. Mixed melting point of this compound with the one prepared from a genuine sample of cineol showed no depression.

*Estimation of Cineol in the Oil.*—To 20 c.c. of the oil was added a 50% solution of resorcinol and the mixture shaken well, when a solid addition compound separated. It was filtered and then decomposed with caustic soda solution when cineol was liberated. It was extracted with ether and after removal of the solvent, the residual liquid was distilled. It measured about 11.3 c.c. The percentage of cineol in the oil is thus 55.9% which agrees with the distillation figures.

*Identification of Cinnamyl Cinnamate in Fraction (II): Hydrolysis.*—A mixture of the fraction (10 c.c.) and a 10% solution of caustic soda (30 c.c.) was refluxed for 3 hours. On cooling, the products of hydrolysis separated into two layers. The layers were separated and extracted with ether. The aqueous layer was acidified with hydrochloric acid, when an acid separated which on recrystallisation from hot water melted at 133° and showed no depression in melting point when mixed with a genuine sample of cinnamic acid. It absorbed bromine. (Found: Neutral equiv., 148.5.  $C_9H_8O_2$  requires neutral equiv., 148).

The ethereal extract was washed with water until free from alkali and dried over anhydrous sodium sulphate. After removal of the solvent, the residual liquid distilled at 255°. A bromo compound was prepared by adding bromine to a solution of the alcohol in chloroform until no more of it was decolorised. A solid compound separated after two days, which melted after recrystallisation from alcohol at 72°. A mixed melting point of this bromo compound with the bromo compound prepared from a pure and genuine sample of cinnamyl alcohol showed no depression.

*Bromine Addition Product of Cinnamyl Cinnamate.*—To the fraction (2 c.c.) was added bromine (1 c.c.), dissolved in ether, and the mixture cooled in a freezing mixture. After 24 hours, crystalline dibromo addition compound separated. On recrystallisation from chloroform it melted at 151°. (Found: Br, 37.5. Calc. for  $C_{18}H_{16}O_2Br_2$ : Br, 37.7 per cent).

*Identification of Methyl Cinnamate in Fraction (III).*—Fraction (III) was hydrolysed like fraction (II) and cinnamic acid in it was identified. The hydrolysis product was a

clear, homogeneous solution unlike as in fraction (II). A part of it was distilled until about one third distilled over. The aqueous distillate on heating with potassium dichromate and sulphuric acid evolved vapours smelling like formaldehyde, suggesting the possibility of methyl alcohol in the distillate.

A bromo compound was prepared by adding bromine to an ethereal solution of the fraction till the colour of bromine persisted. On shaking and keeping for some time a thick crystalline compound separated. On recrystallisation from alcohol it melted at  $117^{\circ}$ . Mixed melting point of this compound with the bromo compound prepared from a genuine sample of methyl cinnamate showed no depression. (Found : Br, 49.3. Calc. for  $C_{10}H_{10}O_2Br_2$ : Br, 49.6 per cent).

CHEMICAL LABORATORIES,  
AGRA COLLEGE, AGRA.

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## COLORIMETRIC DETECTION AND ESTIMATION OF CERIUM

T. K. S. MURTHY AND BH. S. V. RAGHAVA RAO

Quadrivalent cerium gives a bright yellow colour with benzidine in hydrochloric acid solution 0.037 of the element can be detected on a spot-plate. Trivalent rare earths, Th, Cu, Be, Mg, alkaline earths, Zn, Al, Bi,  $\text{UO}_2^{++}$ , Mn, Ni,  $\text{NO}_3'$ ,  $\text{PO}_4'''$ ,  $\text{Cl}'$ ,  $\text{F}'$ ,  $\text{MoO}_4''$ ,  $\text{As}_2\text{O}_4''$ , in moderate amounts do not interfere, but, vanadate and chromate cause interference even in small quantities. The reagent may also be adopted for the colorimetric estimation of cerium.

According to Feigl (*Oesterr. chem. Ztg.*, 1919, 22, 124) quadrivalent cerium gives a green coloration with benzidine in acetic acid solution and by comparative tests with other rare earths Herzfeld (*Z. anal. Chem.*, 1939, 115, 421) showed that the test was specific for cerium and the green colour was noticeable with 0.062 mg. of the element. By far the most sensitive reagent for this element appears to be leucomalachite green (*Mikrochemie*, 1936, 21, 35) which is reported to show the presence of 0.03  $\gamma$  cerium. Other reagents of intermediate sensitivity are known (*Bull. soc. chim.*, 1939, 6, 889; *Z. anorg. Chem.*, 1934, 217, 272; *Ind. Eng. Chem. Anal. Ed.*, 1937, 9, 181; *Helv. Chim. Acta*, 1944, 27, 1479); but in most of these cases the reagent may not be adopted for quantitative estimation. It has been found, however, that benzidine in the presence of hydrochloric acid gives a bright yellow colour with quadrivalent cerium and as little as 0.37 of the element can be easily recognised on a spot-plate. Further, trivalent cerium does not give this reaction and a number of elements, viz., other trivalent rare earths, Th, Cu, Be, Mg, alkaline earths, Zn, Al, Bi,  $\text{UO}_2^{++}$ , Mn, Ni,  $\text{NO}_3'$ ,  $\text{PO}_4'''$ ,  $\text{Cl}'$ ,  $\text{F}'$ ,  $\text{MoO}_4''$ ,  $\text{As}_2\text{O}_4''$ , in moderate amounts do not interfere; but vanadate and chromate cause interference even in small quantities. The presence of large amounts of sulphate should be avoided, since  $\text{SO}_4''$  reacts with benzidine base to form a white crystalline precipitate which would interfere with colour comparison.

The reagent may also be adopted for exact determinations of the element for amounts varying from 0.02 mg. to 0.25 mg. in 50 ml. provided that measurements are made sufficiently quickly, as the yellow colour fades with time. This property also necessitates the use of an external colour standard for comparison.

### EXPERIMENTAL

The following solutions were prepared :

- (i) 0.1% Benzidine in 0.3N hydrochloric acid.
- (ii) About 0.11g. ferric chloride ( $\text{FeCl}_3$ ,  $6\text{H}_2\text{O}$ ) dissolved in 100 ml. of 2N-HCl as the standard for comparison of colour.
- (iii) Standard ceric sulphate containing 0.290 mg. of cerium in 100 ml. of 0.5N sulphuric acid.
- (iv) Test solution in 0.5N sulphuric acid containing 0.4 to 6 mg. of cerium in 100 ml.

To standardise the ferric chloride solution 5 ml. of solution (iii) were taken in a 50 ml. measuring flask; 1 ml. of (i) was added, shaken, and quickly made up to the mark with 3N hydrochloric acid, and compared in a colorimeter.

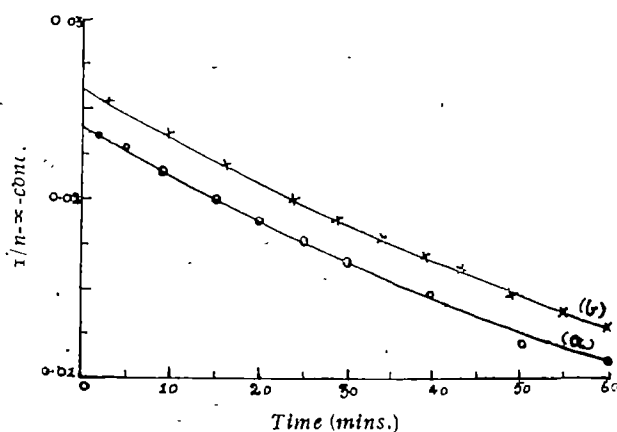


To make an estimation 5 ml. of the test solution were taken in a 50 ml. measuring flask, 1 ml. of the benzidine reagent was added, made up to the mark with 3*N* hydrochloric acid and compared with the standard ferric chloride solution. The following results were obtained with solutions of known cerium content.

TABLE I

Ce taken.	Ce found.	Ce taken.	Ce found.
0.023 mg.	0.022 mg.	0.116 mg.	0.120 mg.
0.035	0.034	0.145	0.145
0.046	0.046	0.174	0.171
0.058	0.059	0.200	0.191
0.125	0.120	0.232	0.231

Fading of the yellow colour with time has also been investigated. In the accompanying diagram the reciprocal of the depth of the colour, which is a measure of the apparent concentration of the element, is plotted against time. Curve (a) refers to a concentration of 0.116 mg. of cerium and curve (b) to 0.125 mg. in 50 ml. It will



be seen that no appreciable error is likely to be introduced if the measurements are concluded within 2 minutes. Curves for various concentrations lie parallel to one another. When the curve is extrapolated to zero time and these latter values are adopted, better agreement with the standard is obtained. The values thus calculated are shown below.

TABLE II

Ce taken	Ce found.	Ce taken.	Ce found.
0.023 mg.	0.023 mg.	0.116	0.117
0.046	0.047	0.125	0.126

## DIPOLE MOMENTS OF METALLIC SOAPS\*

BY BIRENDRA CHANDRA BANERJEE AND SANTI R. PALIT

The dipole moments of six metallic soaps, viz., the oleates of Zn, Cu, Mg, Ni, Pb and Ca have been determined by a heterodyne beat method. The values are 0.29 D, 1.20 D, 1.66 D, 2.67 D, 4.29 D and 4.49 D respectively.

Though the metallic soaps are generally regarded as non-polar from their physico-chemical, particularly solubility behaviour, being highly soluble in organic solvents, these data show them (except Zn) to be fairly highly polar. It is suggested that this high polarity is caused not by a high charge but by a comparatively large separation between the charges owing to the centre of negative charge residing well within the hydrocarbon radical of the oleate.

It is further observed from an examination of the  $\mu$ -values of the group II elements, Mg, Ca and Zn oleates that the order of their dipole moments is opposite to the order of their ionisation potentials.

Calculation of  $\mu$ -values has also been made according to a new equation developed by Jatkar, Sathe and Iyengar. It is found that  $\mu$  (Jatkar *et al.*) is always lower than  $\mu$  (Debye). It is further observed that  $P_2$  (total polarisation) is strongly dependent on concentration both in the new and in the classical Debye equation and so the new equation does not offer any advantage over the Debye equation in these cases.

Attempts have also been made to treat the data by a recently developed simpler method of calculation due to Guggenheim. The method seems to be generally applicable and the  $\mu$ -values are in fair agreement with Debye values.

The metallic salts of long chain fatty acids, which are generally called metallic soaps, have got important applications in industry (vide Elliott, "The Alkaline Earth and Heavy Metal Soaps", Reinhold Publ. Corp., 1946). They are generally used in the manufacture of lubricating grease, waterproofs, driers in paints and varnishes and in various other industrial products (for review vide Lesser, *Soap & Sanitary Chem.*, 1945, 21, 36, 40).

In spite of extensive technical use very few systematic scientific data exist about them, though they are of undoubted interest not only owing to their peculiar physical and chemical properties but also due to their rather unusual type of chemical structure. Great interest has recently been shown about the physico-chemical properties of some of these soaps, particularly their behaviour against organic solvents (Martin and Pink, *J. Chem. Soc.*, 1948, 1750; Gray and Alexander, *J. Phys. Coll.-Chem.*, 1949, 53, 23) and their X-ray structure (Marsden *et al.*, *J. Amer. Oil Chem. Soc.*, 1948, 25, 454; Vold, Hattiangdi and Vold, *J. Coll. Sci.*, 1949, 4, 93).

As opposed to the true soaps quite a few metallic soaps dissolve in pure aromatic and chlorinated hydrocarbons and often dissolve better in mixed solvents (Matiollo, "Protective and Decorative Coatings", John Wiley, 1942, Vol. II, p. 621; Palit, *J. Amer. Oil Chem. Soc.*, 1947, 24, 190; Crawford, *Nature*, 1947, 160, 19) and so they are generally regarded as non-polar though no adequate evidence exists to this

\* Contribution No. 15 from the Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta—12.

point. It was hence thought of interest to carry out measurements of the dielectric constant and dipole moment of these substances, and these data are expected to throw some light on their molecular structure, which in its turn would enable us to explain their properties. This paper reports our results of measurement of dielectric constant and dipole moment of oleates of six bivalent metals, viz., Ca, Mg, Zn, Cu, Ni and Pb by the heterodyne beat method.

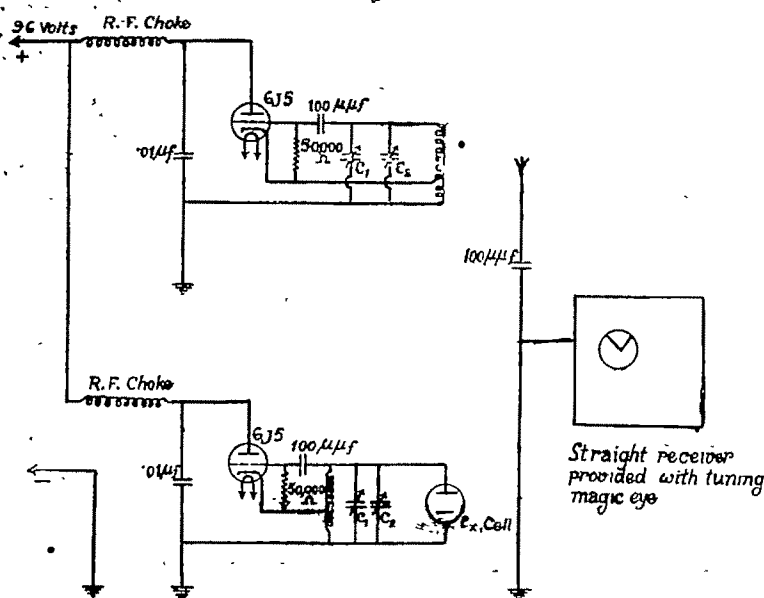
### EXPERIMENTAL

*Preparation.*—The usual method of double decomposition between dilute solution of Na-oleate and a slight excess of metallic salts was adopted in the preparation of metallic oleates. The sodium oleate was dissolved in aqueous butyl alcohol and the metallic salt e.g., acetate (Ca and Pb) or sulphate (Mg, Ni, Zn, Cu) was in pure aqueous solution. The oleates, thus obtained, were washed repeatedly with warm water until completely free from soluble impurities. The product was finally dried in a vacuum oven at  $50^{\circ}$ .

*Solvents.*—Benzene (C. P.) was twice distilled over drierite ( $\text{CaSO}_4$ ) in an all-glass apparatus. The solvent, thus obtained, was dried over sodium.

*Apparatus.*—The heterodyne beat apparatus used in our measurements has been designed and constructed in our laboratory by simplification and modification of a circuit used by Stranathan (*Rev. Sci. Instr.*, 1934, 5, 334; Terman, "Radio Engineering", McGraw Hill, 1947). Two identical oscillators of Hartley type were used. One of the oscillators was kept at a constant frequency and the standardised capacity in the other was varied. In order to overcome the difficulty of frequency drifts in oscillators, the plate voltage was supplied from a dry cell, whereas the filament was heated by a 6-volt storage battery. A variable air condenser provided with a slow motion scale and cali-

Fig. 1



brated against a standard capacitor of a Q-meter in the 400-1000 kilocycle range was used as the standard capacity in our measurement. The beat was detected by a straight receiver provided with a tuning magic eye. The latter device was found to be highly sensitive because even when our ears failed to discriminate extremely low frequency beats, fluttering of the magic eye aided in the accurate adjusting of the variable standardised capacitor against which measurement was made by substitution method. The circuit diagram of the oscillator is shown above.

The measurements were made at room temperature. For this purpose an oil-bath thermostat containing an oil of low dielectric constant was used.

*Experimental Cell.*—The cell was designed in accordance with the directions given by Sauce and Briscoe (*J. Chem. Soc.*, 1925, 315) and modified by Le Fevre and Russel (Le Fevre, "Dipole Moments," Methuen Series, 2nd edition, revised and reset 1948, p. 35; Le Fevre and Russel, *J. Chem. Soc.*, 1936, 491). As regards the silvering of the cell the standard method of reducing ammoniacal silver nitrate by glucose solution was adopted in our case.

*Density Measurement.*—Density of each concentration of the experimental solution was measured by a specific gravity bottle.

*Refractive Index Measurement.*—As the molar refraction of the metallic salts of fatty acids is neither known nor calculable from the standard atomic refraction table, it is found advisable to measure the refractive index for each concentration and then to compute the final result from the following formula:—

$$R_2 = \frac{R_{12} - f_1 R_1}{f_2} = \text{molar refraction for a single solute molecule,}$$

$$\text{where } R_{12} = \frac{n_{12}^2 - 1}{n_{12}^2 + 2} \times \frac{f_1 M_1 + f_2 M_2}{d_{12}} = \text{molar refraction of each solution,}$$

$n_{12}$  = refractive index for Na<sub>D</sub> lines of each solution;  $f_1$  = mol. fraction of the solvent;  
 $d_{12}$  = density of solutions;  $f_2$  = mol. fraction of the solute;

$$R_1 = \frac{n^2 - 1}{n^2 + 2} \times \frac{M_1}{d} = \text{molar refraction of benzene,}$$

$n$  = refractive index of benzene,  $d$  = density of benzene,  $M_1$  = molecular weight of benzene,  
 $M_2$  = molecular weight of the solute used.

In this case it is tacitly assumed that the mixture law is obeyed in the case of molar refraction.

*Method of Calculations.*—If a polar substance is dissolved in a non-polar solvent and the solution is so dilute as to show negligible solvent-solute interaction, the polarisation for that solution is given by

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{f_1 M_1 + f_2 M_2}{d_{12}}$$

where  $\epsilon$  is the dielectric constant of that solution.

If  $P_1$  be the polarisation of the solvent, then assuming the mixture law, the polarisation  $P_{12} = f_1 P_1 + f_2 P_2$ , where  $P_2$  is the polarisation of the solute.

$$\text{Now } P_2 = \frac{P_{12} - f_1 P_1}{f_2}$$

is plotted against  $f_2$  and the polarisation for the single solute molecule corresponding to infinite dilution, i.e.,  $f_2 = 0$  is taken for the calculation of dipole moment because it is at  $f_2 = 0$  that the solute-solute interaction vanishes. The orientation polarisation  $P_{2(\text{orient})}$  is obtained by subtracting  $R_2$  from  $P_2$ . No correction was made for atomic polarisation, as the samples used were not considered to be of such high order of purity as to merit such accurate treatment.

Thus  $\mu = 0.0127 \sqrt{P_{2(\text{orient})} T} \times 10^{-18}$ , where  $T$  = absolute temperature of the bath.

**Dielectric Constant Measurement.**—Dielectric constant was measured by the substitution method. To start with, one of the oscillators was kept fixed and the other was varied by varying the auxiliary as well as the standard capacitor till the beat was zero. This was taken as the initial reading. The experimental cell filled with air was next connected in parallel with the standardised condenser which was adjusted till the beat was just zero. The difference in the two readings give us the capacity due to the cell. The initial reading without the cell, the reading when the cell was filled with air and also the reading with the cell first filled with benzene and then with the experimental solution—these four readings were taken. The dielectric constant for the particular solution was then calculated with the help of the following equation,

$$\epsilon = 2.270 \times \frac{C_{\text{soln}} - C_0}{C_{\text{benzene}} - C_0} = \frac{2.270 \times C_{\text{air}} - C_{\text{benzene}}}{1.270}$$

where  $C_{\text{soln}}$  = capacity of the cell with the interspace filled with dielectric solution;  $C_{\text{benzene}}$  = capacity of the cell filled with benzene and  $C_0$  = zero capacity i.e., capacity of leads, etc.

The dielectric constant of benzene was taken as 2.270 for our measurement. All the data for dielectric constant measurements were taken at a fixed frequency of 600 k. cycles.  $\text{sec}^{-1}$ .

## DISCUSSION

The results of our measurements are presented in Table I. All the metallic soaps studied are observed to have dipole moments which range from almost zero to as high as  $4.5 \times 10^{-18}$ . Of the three second group elements, magnesium, calcium and zinc, it is observed that zinc, which is the highest member of the series, has got the lowest (almost zero) dipole moment. This is probably expected, as the general trend when we go down the periodic table is to form non-polar bonds with organic radicals, which is particularly true of metals of sub-group B. In agreement with the above idea, magnesium, which like zinc easily forms covalent organometallic compounds, e.g. Grignard reagents, is found to have low dipole moment, much lower than that of calcium. In order to test if the dipole moment is determined by the position in the periodic table, we attempted to determine the dipole moment of beryllium and barium

TABLE I  
Temperature = 30°.

Sample.	$f_2$	$\epsilon$	$n_{12}$	$d_{12}$	$P_{12}$	$P_2$ in c.c.	$P_2^a$	$R_{12}$	$R_2$ in c.c.	$R_2/\text{mean}$	$a_D$
Zinc oleate	.00106	2.2770	1.4948	.8658	27.29	242.7		26.65	180.95		
	.00151	2.2735	1.4949	.8654	27.14	225.2	1862c.c.	26.62	188.90	184.42	0.29D
	.00120	2.2720	1.4950	.8650	27.07	216.7		26.57	200.00		
Copper oleate	.00363	2.2840	1.4947	.8672	27.66	250.8		26.89	181.2		
	.00257	2.2780	1.4948	.8662	27.39	237.0	215c.c.	26.73	182.9	185.5	1.2D
	.00213	2.2740	1.4949	.8654	27.28	230.0		26.68	192.50		
	.00128	2.2720	1.4950	.8650	27.09	219.0		26.55	203.10		
Nickel oleate	.00301	2.3170	1.4936	.8656	28.06	428.6		26.76	182.70		
	.00223	2.2950	1.4937	.8650	27.62	372.2	328c.c.	26.25	188.30	182.6	2.67D
	.00153	2.2854	1.4938	.8648	27.33	346.4		26.53	183.00		
	.00102	2.2787	1.4939	.8646	27.16	333.3		26.44	176.50		
Magnesium oleate	.00302	2.2910	1.4946	.8650	27.67	298.0		26.80	182.32		
	.00198	2.2800	1.4947	.8648	27.33	272.7	246c.c.	26.63	181.82	187.62	1.66D
	.00138	2.2760	1.4948	.8646	27.16	253.7		26.55	188.41		
	.00096	2.2730	1.4949	.8644	27.06	250.0		26.49	197.92		
Calcium oleate	.00376	2.3360	1.4947	.8660	28.45	452.0		26.92	183.6		
	.00268	2.3260	1.4948	.8654	28.12	504.0	600c.c.	26.74	182.8	187.7	4.49D
	.00185	2.3150	1.4949	.8650	27.83	557.0		26.63	189.2		
	.00128	2.3040	1.4950	.8646	27.55	578.0		26.54	195.3		
Lead oleate	.00152	2.2890	1.4937	.8684	27.36	368.42		26.48	131.58		
	.00102	2.2849	1.4938	.8668	27.26	431.40	504c.c.	26.43	127.45	126.88	4.29D
	.00074	2.2829	1.4939	.8656	27.17	459.46		26.40	121.62		

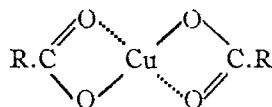
oleates. Unfortunately, however, we did not meet with much success as both these oleates were found to be too insoluble in the common solvents to admit of direct dipole

moment measurement. We have, however, lately obviated the above difficulty by using benzene-alcohol mixture as the solvent and applying Guggenheim's method of calculation, the results of which would constitute a future publication.

It will be noted that (from Table I) of the six soaps, the  $P_2$  versus  $f_2$  curves show the usual positive slopes for all soaps except that of calcium and lead which latter show negative slope. In other words, the latter soaps are more polar in dilute solution. It is believed that this behaviour is at least in part caused by the strong association tendency of these soap molecules to form micelles at higher concentration.

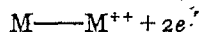
Of the transition elements, we have studied nickel and copper oleate. It will be observed from the figure that nickel has a fairly high dipole moment, 2.67  $D$  and copper oleate has got somewhat less moment, 1.20  $D$ , but has a value higher than its right hand neighbour, zinc. It is quite surprising that these substances, which are so highly soluble in hydrocarbon solvents, have such high dipole moments.

The question of geometry and polarity of the molecule naturally arises in connection with the dipole moment. For example, if the bivalent oleates have completely symmetrical structures, it is difficult to see how they give rise to such high moments at all. From these values we would suggest that the structure of these oleates is not symmetrical, the two valencies not being distributed in opposition to each other so as to annul the effect of each other. Further, it is quite likely that pseudo rings are formed as shown below by each of the fatty acids and these two rings by the exercise of co-ordinate valency between the two oxygen atoms and the central copper atom may not lie in the same plane. The most plausible disposition would be the four oxygen atoms tetrahedrally arranged round the copper atom.



The metallic soaps, for example, the nickel and copper oleates, have a very high solubility in hydrocarbon solvents and these solutions do not conduct current. From these it is generally assumed that these metallic soaps are non-polar compounds. In fact, there is no doubt from chemical standpoint that the bond between copper and the organic radical should be weakly ionic, if at all. The dipole moment data are, however, inconsistent with these chemical evidences. These two views can be reconciled if we postulate that the centre of negative charge of these metallic soaps must reside well inside the hydrocarbon part of the molecule. In fact, we may conceive that the negative charge in the oleate anion is distributed over the whole ion so that the centre of gravity of the charge lies further from copper which might explain the high dipole moment, though the polarity of the bond may not be so high, since dipole moment involves the product of two quantities, charge and their separation. The mechanism of the distribution of the negative charge is probably a simple inductive effect. The negative charge of the  $\text{COO}^-$  end will polarise each of the  $\text{C-H}$  bond by repulsion of the electrons, the more, the nearer the carbon atom, and this will in effect make the negative charge distribute over the whole hydrocarbon radical of the soap molecule.

Since the polarity of the metal-organic bond is caused by a displacement of the two valency electrons from the metal to the oleic acid radical, it seems reasonable that the dipole moment values will follow inversely the ionisation potential of the metal *i.e.*, if the energy required for the reaction,



is low, the dipole moment will be high and *vice versa*. This correlationship of course will not exist for salts of lower acids because the molecules being small, specific electrical disturbances will tend to mask such a relationship. In the following table have been compiled the values of the observed dipole moments and ionisation potentials. (taken from International Critical Tables). It will be observed that the expected relationship exists at least qualitatively among the elements of the same group of the periodic table (Group II). Copper and lead which belong to a different group (Group I), however, do not exactly fit in the above series. Only more work can show whether this inverse parallelism is mere accidental or not.

TABLE II

Soap.	Dipole moment.	Ionisation potential $M \longrightarrow M^{++} + 2e$ .
Calcium oleate	4.49 D	17.91 volts
Magnesium oleate	1.66	22.58
Zinc oleate	0.29	27.25

*Jatkar's New Equation.*—Following an essentially Debye's method of calculation but with some imposed quantum restrictions on orientation of the dipoles in the electric field, Jatkar, Iyengar and Sathe (*J. Indian Inst. Sci.*, 1946, **28A**, Part II, 1) have recently developed a new equation to replace Debye's equation. These authors claim superiority of their equation on various points of which they mention that the concentration variation of  $P_2$  values will be smaller or negligible. We have recalculated all our values using this new equation and the  $\mu$ -values are given in Table IV. These new  $\mu$ -values, as found by Jatkar and his associates, are somewhat less than the Debye's value, and our calculations also show this to be so. This new equation by the above authors is

$$P = \frac{(\epsilon - 1)M}{d}$$

$$\text{Electronic polarisation} \quad P_e = \frac{(n^2 - 1)}{d}$$

$$P_{12} = \frac{(\epsilon - 1)(M_1 f_1 + M_2 f_2)}{d_{12}} = P_1 f_1 + P_2 f_2 \text{ and}$$

$$P_2 - P_e = \frac{4\pi N \mu^2}{kT}$$



TABLE III

*Dipole moments by Guggenheim's methods*

Sample.	C (moles/c.c.).	$\epsilon - n^2$ .	$\Delta$ .	$\Delta/C$ .	$(\Delta/C)c \rightarrow 0$ .	$\mu$ .
Zinc oleate	$2.253 \times 10^{-5}$	0.0426	0.0082	$3.640 \times 10^3$	0	0
	$1.656 \times 10^{-5}$	.0388	.0044	$2.657 \times 10^3$		
	$1.314 \times 10^{-5}$	.0370	.0026	$1.980 \times 10^3$		
	0	.0344				
Copper oleate	$3.938 \times 10^{-5}$	.0499	.0164	$4.164 \times 10^3$	$1.72 \times 10^3$	$1.18 \times 10^{-18}$
	$2.798 \times 10^{-5}$	.0436	.0101	$3.609 \times 10^3$		
	$1.940 \times 10^{-5}$	.0393	.0058	$2.989 \times 10^3$		
	$1.402 \times 10^{-5}$	.0370	.0035	$2.497 \times 10^3$		
	0	.0335				
Magnesium oleate	$3.287 \times 10^{-5}$	.0572	.0228	$6.94 \times 10^3$	$2.40 \times 10^3$	$1.60 \times 10^{-18}$
	$2.170 \times 10^{-5}$	.0459	.0115	$5.30 \times 10^3$		
	$1.517 \times 10^{-5}$	.0416	.0072	$4.75 \times 10^3$		
	$1.057 \times 10^{-5}$	.0383	.0039	$3.70 \times 10^3$		
	0	.0344				
Nickel oleate	$1.268 \times 10^{-5}$	.0862	.0488	$14.930 \times 10^3$	$5.9 \times 10^3$	$2.19 \times 10^{-18}$
	$2.266 \times 10^{-5}$	.0539	.0265	$11.690 \times 10^3$		
	$1.666 \times 10^{-5}$	.0540	.0166	$9.963 \times 10^3$		
	$1.113 \times 10^{-5}$	.0470	.0096	$8.626 \times 10^3$		
	0	.0374				
Lead oleate	$1.672 \times 10^{-5}$	.0579	.0205	$12.27 \times 10^3$	$19.8 \times 10^3$	$4.01 \times 10^{-18}$
	$1.125 \times 10^{-5}$	.0535	.0161	$14.31 \times 10^3$		
	$0.823 \times 10^{-5}$	.0512	.0138	$15.92 \times 10^3$		
	0	.0374				
Calcium oleate	$4.071 \times 10^{-5}$	.1019	.0684	$16.80 \times 10^3$	$29.3 \times 10^3$	$4.873 \times 10^{-18}$
	$2.863 \times 10^{-5}$	.0916	.0581	$26.30 \times 10^3$		
	$2.024 \times 10^{-5}$	.0813	.0468	$23.12 \times 10^3$		
	$1.411 \times 10^{-5}$	.0690	.0355	$25.16 \times 10^3$		
	0	.0335				

TABLE IV

Sample.	$\mu$ (Debye).	$\mu$ (Guggenheim).	$\mu$ (Jatkar).
Zinc oleate	0.29 D	0 D	0.22 D
Copper oleate	1.20	1.18	1.07
Magnesium oleate	1.66	1.60	1.39
Nickel oleate	2.67	2.19	2.34
Lead oleate	4.29	4.01	3.22
Calcium oleate	4.49	4.87	3.78

As far as our data go, this new equation is not found to offer any advantage or disadvantage over the classical Debye equation; the variation of  $P_2$  with concentration being of the same order, if not more, with this new equation as that obtained from the classical equation.

**Guggenheim's Method of Calculation.**—Very recently Guggenheim (*Trans. Faraday Soc.*, 1949, **45**, 714) has proposed a simple and straight forward method of calculating  $\mu$ . His method requires very accurate dielectric constant and refractive index values but requires only density values of ordinary accuracy. This is a great experimental advantage in working with volatile solvents. Guggenheim's method consists in finding the slope of the  $\epsilon - n^2$  versus  $C$  (moles per c.c.) curve which should be a straight line if the mixture laws for refractivity and polarisation are valid. This slope is equated to the following expression

$$\text{Slope} = \frac{(\epsilon_0 + 2)(n_0^2 + 2)}{3} \cdot \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT}$$

$$\text{i.e., } \mu_{\text{Guggenheim}} = 0.0127 \sqrt{\frac{3T \times \text{slope}}{(\epsilon_0 + 2)(n_0^2 + 2)}} \times 10^{-18}$$

Evidently, the intercept of the above curve on the  $y$ -axis would be equal to  $\epsilon_0 - n_0^2$  and so would be the same for all solutes in the same solvent. In attempting to apply this method to our data we find that the points fall fairly well on a straight line having a common intercept at the actually observed value of  $\epsilon_0 - n_0^2$ . There is, however, much uncertainty in finding the slope and to obviate the uncertainty of finding the slope we have, following Guggenheim, first calculated  $\Delta$  as given below. Next  $\Delta/C$  is plotted against  $C$  and extrapolated  $C=0$ .  $\mu$  is then calculated from the equation given below:

$$\Delta = (\epsilon - n^2) - (\epsilon_0 - n_0^2)$$

$$\mu = 0.0127 \times 10^{-18} \sqrt{\frac{3T(\Delta/C)_{C=0}}{(\epsilon_0 + 2)(n_0^2 + 2)}}$$

The results of our calculation are presented in Table III and a comparison is made with  $\mu$ , calculated, by Debye's method, in Table IV. We have found that much labour in calculation is saved by using Guggenheim's method. It is further to be pointed out that since each point on the graph is based on both dielectric constant and refractive index, the errors in both have more chance to cancel out from the final result, whereas in Debye's method of calculation differences of two large quantities, viz.,  $P_{12} - P_1 f_1$  and  $(P_2)_\infty - (R_2)_\infty$  are involved introducing uncertainty in the final result.

It will be observed that the agreement between  $\mu_{\text{Debye}}$  and  $\mu_{\text{Guggenheim}}$  is fairly good for all soaps except those of lead and calcium. Perhaps the larger extrapolation needed for these two soaps and also their anomalous concentration variation of polarisation, as already pointed out, may contribute to this larger difference.

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DEPARTMENT OF PHYSICAL CHEMISTRY,  
INDIAN ASSOCIATION FOR THE CULTIVATION OF  
SCIENCE, CALCUTTA.

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## ZIRCONIUM: ITS ESTIMATION AND SEPARATION. HYDRAZINE SULPHATE

BY CH. VENKATESWARLU AND Bh. S. V. RAGHAVA RAO

Hydrazine sulphate precipitates zirconium completely from solutions of  $p_H$  2.8 and above. This reagent also separates the element from Be, Ni and rare earths in the  $p_H$  range 2.8 to 3.0 in a single precipitation. Separation from thorium is more delicate and the  $p_H$  is critical at 2.8.

During an investigation into the analytical behaviour of zirconium, it has been observed that hydrazine sulphate, while precipitating the element quantitatively from solution of  $p_H$  2.8 and above, provides a method for its separation from certain elements associated with it, particularly thorium and cerite earths.

### E X P E R I M E N T A L

*Estimation of Zirconium.*—Two stock solutions of pure zirconyl chloride in 0.1N-HCl were prepared and the zirconium was determined by precipitation with *m*-nitrobenzoic acid and subsequent ignition to  $ZrO_2$ ; 0.0486 g. and 0.0560 g. of  $ZrO_2$  were found in 20 ml. of the two solutions respectively. The same estimations were carried out precipitating with hydrazine sulphate. The zirconium solutions (20 ml.) were first neutralised to Congo red with 0.1N ammonia; 5 drops of 0.1N-HCl were next added and diluted to 350 ml. 5% Hydrazine sulphate solution (50 ml.) was then added. The white precipitate of hydrated zirconia was allowed to settle on a water-bath for about 10 minutes after which it was cooled and filtered, washed first with 0.5% hydrazine sulphate and finally with water and ignited. Experimental values of  $ZrO_2$  found (0.0485 g. and 0.0562 g.) are in excellent agreement with standard values

*Separation: (a) From Thorium.*—Thorium when present singly is not precipitated until the  $p_H$  falls to 4.8. Further hydrazine sulphate appears to exercise an inhibitory influence on the precipitation of thorium by oxalic acid. In an experiment only 0.0750 g. of  $ThO_2$  was found in place of 0.0873 g. taken.

When admixed with zirconium, however, co-precipitation of thorium occurs even at  $p_H$  3.0. Results obtained under varying conditions of  $p_H$  are shown in Table I.

TABLE I

*Effect of  $p_H$  on the separation of zirconium from thorium.*

ZrO <sub>2</sub> taken = 0.0486 g ThO <sub>2</sub> added = 0.876 g											
Expt. No.	...	1	2	3	4	5	6	7	8	9	10
p <sub>H</sub>	...	3.4	3.2	3.0	2.8	2.8	2.7	2.6	2.4	2.2	2.2
ZrO <sub>2</sub> (found in g.)		0.0622	0.0568	0.0522	0.0487	0.0485	0.0480	0.0470	0.0449	0.0433	0.0435

Residue corresponding to experiment 1 was fused with sodium bisulphate<sup>3</sup> and the zirconium was estimated with mandelic acid (Kumins, *Z. anal. Chem.*, 1947, 19, 376).

ZrO<sub>2</sub> found was 0.0484 g. showing that all the zirconium was precipitated and the excess weight was due to thorium only that was coprecipitated. This was further confirmed by tests on the filtrate for zirconium. The filtrate was concentrated to a small volume by evaporation to 50 ml. H<sub>2</sub>SO<sub>4</sub> (10 ml.), 3% H<sub>2</sub>O<sub>2</sub> (10 ml.) and sodium hydrogen phosphate failed to show any turbidity which would have been produced in the presence of 0.1 mg. of ZrO<sub>2</sub>.

To the mixed solution of zirconium and thorium chlorides 5% hydrazine sulphate (100 ml.) was added and diluted to about 200 ml. The  $p_H$  was adjusted to 2.8 and kept on a water-bath for 1½ hours. It was then allowed to cool and collected on Whatman No. 42 filter, washed with 0.5% hydrazine sulphate and finally with water. It was ignited and weighed.

(b) *From other Elements.*—Separation from other elements, viz. Be, Ni and rare earths is more simple. The procedure outlined for the determination of zirconium was employed. Iron was reduced and the precipitation of zirconium was not complete. In the presence of aluminium some zirconium was held in solution. Uranium, tin, and titanium were precipitated along with zirconium. Results obtained are given in Table II.

TABLE II

	ZrO <sub>2</sub> (taken)	Elements added	ZrO <sub>2</sub> (found)	Difference.
1.	0.0486 g.	R <sub>2</sub> O <sub>3</sub> 0.2004 g	0.0486 g.	0.0000 g.
2.	—	— 0.4008	0.0485	-0.0001
3.	—	Ni 0.4012	0.0488	+0.0002
4.	—	BeO 0.3786	0.0485	-0.0001
5.	—	ThO <sub>2</sub> 0.0876	0.0488	+0.0002
6.	—	— 0.1752	0.0486	-0.0000
7.	0.0562	— 0.0876	0.0562	0.0000
8.	—	— 0.1752	0.0564	+0.0002

## CONCLUSION

Hydrazine sulphate precipitates zirconium quantitatively in solutions of  $p_H$  2.8 and higher. Separation from thorium in a single precipitation is effective at  $p_H$  2.8. This is rather critical. Separation from Be, Ni and rare earths can be accomplished over a wider  $p_H$  range, 2.8 to 3.0.

CHEMISTRY DEPARTMENT,  
ANDHRA UNIVERSITY,  
WALTAIR.

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STUDIES ON SULPHONAMIDES AND ANALOGOUS COMPOUNDS.  
PART V. N<sup>4</sup>-SUBSTITUTION

By U. P. BASU, SUDHAMOY MUKHERJEE AND A. N. BOSE

Characteristic differences in sulphacetamide and sulphanilylbenzamide after substitution of the *p*-amido hydrogen by phthalyl radical have been studied and discussed.

As the basic amino group in sulfa drugs plays a vital part in producing bacteriostasis, attempts are often being made to produce their N<sup>4</sup>-substituted derivatives in order to lower their toxicity and/or to widen their activity. The drug action is believed to be due to the formation of a drug-enzyme complex with the enzyme of the pathogenic organisms, and any difference in the activity between the two drugs is ascribed to be due to the relative dissociation constants of sulphonamide-enzyme complexes formed at the body  $p_H$  (cf. Klötz, *J. Amer. Chem. Soc.*, 1944, **66**, 459; Woods, *Brit. J. Exp. Path.*, 1940, **21**, 74; Sevag, *Adv. Enzymol.*, 1946, **6**, 33). But as no definite idea is yet known about the various complex enzyme systems, numerous derivatives of sulfa compounds are being prepared in the expectation of isolating a compound which may reach the site of infection in adequate concentration (cf. Poth and Ross, *J. Lab. Clin. Med.*, 1944, **29**, 785; Bonchart, *J. Dig. Med.*, 1946, **18**, 629; Basu, this *Journal*, 1949, **26**, 130).

In the course of our investigations phthalylsulphacetamide and phthalylsulphanilylbenzamide (Sikdar and Basu, this *Journal*, 1945, **22**, 345) were prepared and their solubility in water and that again in presence of a phosphate buffer, their dissociation exponent and bacteriostatic activity were studied and the results recorded in this paper. The former compound has been recently noted to be clinically effective in typhoid fever (cf. Wright, *Canad. Med. Assoc. J.*, 1949, **61**, 63).

EXPERIMENTAL

**N<sup>4</sup>-Phthalylsulphacetamide.**—A mixture of sulphacetamide (10.7 g.) and freshly sublimed phthallic anhydride (7.4 g.) was dissolved in acetone (40 c.c.) with shaking. The solution was filtered and the filtrate was left aside at the room temperature (25-26°); crystals began to separate out and were collected after a few hours. They were recrystallised from alcohol in fine prismatic needles, m.p. 202°. (Found: N, 7.6. C<sub>16</sub>H<sub>14</sub>O<sub>6</sub>N<sub>2</sub>S requires N, 7.74 per cent). The substance is insoluble in ether, and sparingly soluble in boiling water. It, however, dissolves readily in sodium bicarbonate solution and may be precipitated out on acidification with dilute acid. The compound is very susceptible to hydrolysis and is readily hydrolysable in presence of dilute alkali to *p*-aminobenzene sulphonacetamide.

**N<sup>4</sup>-Phthalylsulphanilylbenzamide.**—The compound used in the course of this investigation was prepared by the method previously described (Sikdar and Basu, *loc. cit.*) and was found to melt at 224-25°.

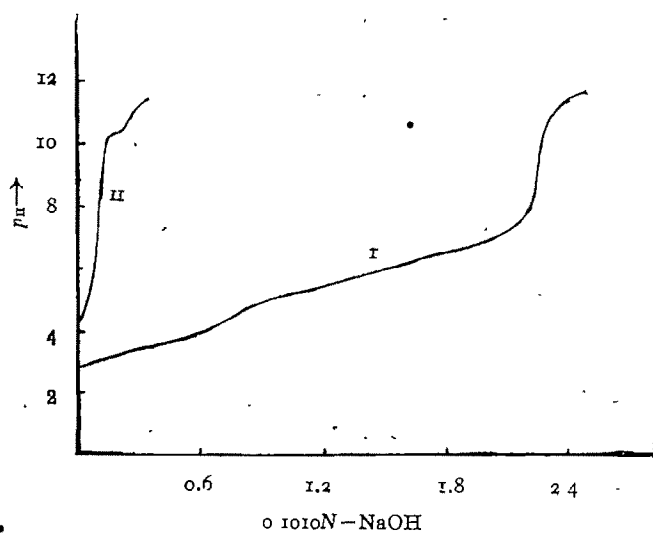
*Physical Characteristics.*—A study has been made of some physical and chemical properties of phthalylsulphacetamide and phthalylsulphabenzamide. Solubilities were determined in water and in 0.2 *M* phosphate buffer solutions. The aqueous solutions were also titrated potentiometrically with caustic soda solution. The data are given in Table I.

TABLE I

Particulars.	Phthalylsulphacetamide	Phthalylsulphabenzamide
Solubility in water (at 30°).	110 mg./100 c.c. $p_H=2.8$	mg / 100 c.c. $p_H=4.38$
Solubility in phosphate buffers	436 mg./100 c.c. $p_H=4.19$ 910 mg./100 c.c. $p_H=5.53$	154 mg./100 c.c. $p_H=5.57$ 705 mg./100 c.c. $p_H=5.88$
Dissociation exponent calculated from $p_H$ at half neutralisation	$pK_{a_1}=3.86$ ( $pK_{a_1}$ for phthalic acid=2.9)	( $pK_{a_1}$ for sulphabenzamide=4.57)
Dissociation exponent for the second stage of neutralisation from half neutralisation	$pK_{a_2}=5.3$ ( $pK_{a_2}$ for sulphacetamide=5.38)	$pK_{a_2}=8.52$
Dissociation exponent for the 3rd stage	$pK_{a_3}=6.6$ ( $pK_{a_3}$ for phthalic acid=5.51)	$pK_{a_3}=9.93$
Appearance of aqueous solution	Clear	Opalescent

The potentiometric titration curve (curve I in Figure 1) for sulphacetamide has two breaks, the first inflexion occurring on the addition of exactly one-third of the amount of alkali required at the final inflexion. The compound thus appears to behave as a tribasic acid in which the second and third stages of neutralisation overlap each other so that the second break in the curve is not perceptible. The first stage of neutralisation

FIG. 1



Curves I and II refer respectively to phthalyl-sulphacetamide and  $\alpha$ -sulph-benzamide.

corresponds to a  $p_{ka}$  value 3.32 calculated from the  $p_n$  at half neutralisation using the equation,

$$p_k = p_n + \log \frac{C - [B] - [H^+] + \frac{k_w}{[H^+]}}{[B] + [H^+] - \frac{k_w}{[H^+]}}$$

This value is somewhat higher than the dissociation exponent of phthalic acid for which  $p_{ka}$  is 2.9. For the second stage, the value of  $p_{ka}$  calculated in the same way, is 5.31, which agrees closely with that for sulphacetamide, namely, 5.38. The value of  $p_{ka}$  for the third stage comes to 6.6.

It may be supposed that the first stage represents the neutralisation of the free carboxyl group of phthalic acid, this bearing the strongest acid group. The second stage appears to correspond to a neutralisation of the replaceable hydrogen atom in the sulphamido group of sulphacetamide in view of the close agreement between the dissociation constants. During the third stage of neutralisation, the gradual hydrolytic breakdown of the phthalimido group and the simultaneous neutralisation of the second carboxyl group of phthalic acid with alkali may be envisaged. The apparent dissociation exponent under these conditions would be higher than the true value for the free acidic group, as is actually found to be the case (i.e., 6.6 in place of 5.51).

The hydrolytic breakdown, supposed to occur at the third stage, would be accompanied with the regeneration of the free amino group and the formation of alkali phthalate. Diazo reaction using sodium nitrite and  $\beta$ -naphthol actually confirmed the presence of the free amino group. The unneutralised solution of the phthalyl compound did not respond to this test.

From the merging of the second and the third stages of neutralisation it may be inferred that the hydrolytic breakdown sets in even during the second stage. This was also confirmed by the diazo test when the solution at  $p_n$  6.0 gave a somewhat feeble coloration. This  $p_n$  corresponds to the completion of the second stage of neutralisation in the titration curve.

The titration curve for phthalylsulphabenzamide (curve II) shows essentially similar features, the first inflexion point corresponding to one third of the amount of alkali added at the second and final inflexion. Here also the second and third stages of neutralisation overlap. The  $p_k$  values corresponding to the three stages are 5.13, 8.53 and 9.93. If the three stages represent, as postulated in the other case, respectively the neutralisation of the free carboxyl of the phthalic acid, that of the dissociable hydrogen atom, and the hydrolysis of the phthalyl group, it follows that the ionisations of the acidic groups have been depressed much more here than in the case of phthalylsulphacetamide.

**Bacteriostatic Activity.**—The bacteriostatic activity of the compounds was studied against the organisms as recorded in Table II. Each of the drugs was incorporated in 1% peptone water ( $p_n$  7.5) in requisite concentration.



TABLE II

Culture: 18 hours in 1% peptone water. Inoculum=500 cells in each case. Incubation temp. = 37.0°. Period of observation = 72 hrs.

Figures indicate minimum bacteriostatic concentration in mg. per 100 c.c. of the medium.

Compounds.	Organisms				
	<i>E. Typhosa.</i>	<i>Para Typhi B.</i>	<i>Sonnei.</i>	<i>Flexner Y.</i>	<i>B. Pyocyane.</i>
Sulphacetamide	<50 >25	50	12.5	25	25
Sulphanilylbenzamide	„	50	<6.25	<6.25	100
Phthalylsulphacetamide	„	50	6.25	6.25	12.5
Phthalylsulphanilylbenzamide	„	50	<6.25	6.25	25

From Table II it would be noticed that all the compounds are equally effective against *E. typhosa* and *S. paratyphi B.* They are more bacteriostatic against dysentery organism. The enhanced activity of phthalylsulphacetamide against *B. Pyocyane* may also be noticed.

The ready susceptibility of the phthalylsulphacetamide to hydrolysis in alkaline condition may set up a condition in the system that will be responsible for its reported activity in typhoid infections. The compound is being clinically evaluated.

## SUPERSATURATION OF LIQUIDS IN LIQUIDS

BY RAM GOPAL AND R. P. RASTOGI

The limits of supersaturation of liquids in liquids have been studied both from theoretical and practical standpoint. It is shown that if the interfacial tension between the two participating components is sufficiently high and relative internal pressures nearly equal, definite and appreciable limits of supersaturation can be obtained.

Supersaturation of liquids in liquids still appears to be a controversial topic, and it is almost impossible to obtain a piece of convincing evidence on the either side in the literature. Rothmund (*Z. physikal. Chem.*, 1898, **26**, 443) considered the possibility of existence of such solutions although experimentally he met with negative results, a fact also supported by the experiments of Fawcett (Thesis, University of Toronto, 1912). On the other hand, the experiments of Fuchtbauer (*Z. physikal. Chem.*, 1904, **48**, 566) gave strong evidence of existence of supersaturation although it was found to be still very low and was accounted to be "due to presence of dust particles or foreign nuclei of some sort, perhaps colloids." In order to settle these conflicting views Davis (*J. Amer. Chem. Soc.*, 1916, **38**, 1166) measured supersaturation in a few systems, and concluded that the supersaturation of liquids in liquids was a reality. But the degrees of supersaturation obtained by him are very small and do not appear to present any convincing proof of the existence of supersaturation.

The phenomenon of supersaturation in solid-liquid systems has been investigated in this laboratory for the last several years with a special technique\* discussed in a previous communication (this *Journal*, 1943, **20**, 183). It is proposed to apply the same technique in liquid-liquid systems to ascertain if any reliable supersaturation can be obtained.

A very important aspect of supersaturation of liquids in liquids that attracts our attention is that the interfacial tension (at least in bulk) between two liquids can be easily found out either experimentally or calculated from Antonow's rule for sparingly soluble liquids. Thus, it will be possible to examine the equation,

$$T_s - T = \frac{2M\sigma}{\rho\lambda\gamma} T_s$$

(or any other similar expression which would hold in liquids) which up to this time eluded all attempts towards a thorough examination. Besides, Kenrick's conception (University of Toronto Studies, 1913, 99, 4) that the small degree of supersaturation of liquids is connected with small interfacial tension between liquids and that there is no essential difference between supersaturated solutions of solids in liquids and those of liquids in liquids, may be tested in a more precise manner than have been done up to this time.

\* This cannot be claimed to be a very accurate method but at least it avoids disturbing influences to a large extent

We shall first try to deduce a suitable relationship for supersaturation for liquid-liquid systems. The solubility of liquids in liquids has been theoretically deduced by Hildebrand (*J. Chem. Phys.* 1933, 1, 817), Scatchard (*Chem. Rev.*, 1931, 8, 321; *J. Amer. Chem. Soc.*, 1935, 57, 1805) and others. A simplified form of their expression for low solubility, according to Black, Joris and Taylor (*J. Chem. Phys.*, 1948, 16, 541) is

$$RT \ln \frac{\alpha_1}{N_1} = V_1 \left[ \left( \frac{\partial E_1}{V_1} \right)^{\frac{1}{2}} - \left( \frac{\partial E_2}{V_2} \right)^{\frac{1}{2}} \right]^2 \quad \dots \quad (1)$$

where  $\alpha_1 = f/f_0$ ,  $f$  being the fugacity of the solute in solution and  $f_0$ , the fugacity of the pure solute;  $N_1$  and  $V_1$  denote the molar concentration and molar volume of the solute;  $\partial E_1$  and  $\partial E_2$  are the heats of vaporisation of solute and the solvent, and hence  $\partial E_1/V_1$  and  $\partial E_2/V_2$  represent approximately the respective internal pressures.

In dilute solutions (i.e. sparing solubility)  $\alpha_1$  may be taken to be unity. Therefore (1) reduces to

$$\begin{aligned} -RT \ln N_1 &= V_1 \left[ \left( \frac{\partial E_1}{V_1} \right)^{\frac{1}{2}} - \left( \frac{\partial E_2}{V_2} \right)^{\frac{1}{2}} \right]^2 \\ \text{or } \ln N_1 &= - \frac{V_1}{RT} \left[ \left( \frac{\partial E_1}{V_1} \right)^{\frac{1}{2}} - \left( \frac{\partial E_2}{V_2} \right)^{\frac{1}{2}} \right]^2 \quad \dots \quad (2) \end{aligned}$$

Combining (2) with the equation of Thompson, viz.,

$$RT \ln \frac{Pr}{P_\infty} = \frac{2M\sigma}{\rho r} \quad \text{or} \quad RT \ln \frac{Sr}{S_\infty} = \frac{2M\sigma}{\rho r}$$

one gets at  $T$

$$\begin{aligned} \ln Sr(T) &= \frac{2M\sigma}{\rho r RT} + \ln S_\infty \\ &= \frac{2M\sigma}{\rho r RT} + \ln N_1 \\ \text{or } Sr(T) &= A \text{ Exp. } \left[ \frac{2M\sigma}{\rho r RT} - \frac{V_1}{RT} \left\{ \left( \frac{\partial E_1}{V_1} \right)^{\frac{1}{2}} - \left( \frac{\partial E_2}{V_2} \right)^{\frac{1}{2}} \right\}^2 \right] \end{aligned}$$

Similarly at  $T + \partial T$

$$Sr(T + \partial T) = A \text{ Exp. } \left\{ \frac{2M(\sigma + \partial\sigma)}{R(T + \partial T)(r + \partial r)(\rho + \partial\rho)} - \frac{V_1}{R(T + \partial T)} \left[ \left( \frac{\partial E_1}{V_1} \right)^{\frac{1}{2}} - \left( \frac{\partial E_2}{V_2} \right)^{\frac{1}{2}} \right]^2 \right\}$$

Equating  $Sr(T)$  and  $Sr(T + \partial T)$ , as in solid-liquid systems, and putting for convenience

$$\left[ \left( \frac{\partial E_1}{V_1} \right)^{\frac{1}{2}} - \left( \frac{\partial E_2}{V_2} \right)^{\frac{1}{2}} \right]^2 = I$$

one obtains

$$\frac{2M\sigma}{\rho r RT} - \frac{V_1 I}{RT} = \frac{2M(\sigma + \partial\sigma)}{R(T + \partial T)(\rho + \partial\rho)(r + \partial r)} - \frac{V_1 I}{R(T + \partial T)} \quad \dots \quad (4)$$

$$\text{or } \frac{2M\sigma}{\rho r T} - \frac{V_1 I}{T} = \frac{2M(\sigma + \partial\sigma)}{(T + \partial T)(\rho + \partial\rho)(r + \partial r)} - \frac{V_1 I}{(T + \partial T)} \quad \dots \quad (4)$$

Simplifying and neglecting infinitesimals of higher order than first (4) reduces to

$$2 \left[ \frac{\partial r}{r} + \frac{\partial \rho}{\rho} + \frac{\partial T}{T} - \frac{\partial \sigma}{\sigma} \right] = \frac{I r}{\sigma} \left[ \frac{\partial \rho}{\rho} + \frac{\partial T}{T} \right] \quad \dots \quad (5)$$

$$\text{But } \frac{\partial \rho}{\rho} = \frac{\partial \sigma}{\sigma} \quad (\text{approx.})$$

$$\text{Therefore } 2 \left[ \frac{\partial r}{r} + \frac{\partial T}{T} \right] = \frac{I r}{\sigma} \left[ \frac{\partial \rho}{\rho} + \frac{\partial T}{T} \right] \quad \dots \quad (6)$$

Now  $\partial\rho/\rho$  is very small as compared to  $\partial T/T$ , and therefore it can be neglected in comparison to  $\partial T/T$ . Equation (6) now becomes

$$2 \left[ \frac{\partial r}{r} + \frac{\partial T}{T} \right] = \frac{I r}{\sigma} \cdot \frac{\partial T}{T}$$

$$\text{i.e. } \int \frac{\partial T}{T} = \int \frac{2\sigma}{r(Ir - 2\sigma)} \partial r$$

which on integration and suitable transformations yields

$$T = C \left[ I - \frac{2\sigma}{r} \right] \quad \dots \quad (7)$$

Applying the condition that at  $T = T_s$ ,  $r = \infty$ , one gets

$$C = \frac{T_s}{I} \quad \dots \quad (8)$$

which when combined with (7) results in

$$T_s - T = \frac{2\sigma T_s}{I r} = \frac{2\sigma T_s}{I r} \cdot \left[ \left( \frac{\partial E_1}{V_1} \right)^{\frac{1}{2}} - \left( \frac{\partial E_2}{V_2} \right)^{\frac{1}{2}} \right]^2 \quad \dots \quad (9)$$

Choosing  $T_s$  to be the same in different systems Eq. (9) shows that  $T_s - T$  varies directly as  $\sigma$  and inversely as  $I$ , if  $r$  is assumed to be constant. Hence, in order to get appreciable supersaturation  $\sigma$  must be as large as possible and  $I$  as small as possible, but not zero, for then r. h. s. of (9) will become infinitely great i.e. supersaturation will be infinite. This happens when liquids are miscible in all proportions for which a necessary condition is that the constituents should have similar internal pressures.

#### EXPERIMENTAL

The substances used were purified by standard methods and tested for purity in the usual manner (cf. Vogel, "A Text-book of Practical Organic Chemistry", 1946). Known amounts of liquids were weighed out in special test tubes (this *Journal*, 1943,

20, 183) and the required amount of the liquid solvent was added from a graduated pipette (*loc.cit.*). The tubes were sealed and heated under water in a beaker of suitable size. The beaker was heated to a temperature of about 5°-10° higher than the saturation temperature. The beaker was allowed to cool slowly (*loc.cit.*). The temperature of spontaneous separation of the solute was taken as the temperature at which the cloud appeared. This happened, in general, almost simultaneously throughout the system. The saturation temperature  $T_s$  was verified by finding out the temperature at which the cloud disappeared and reappeared. The results obtained are given in Table I.

TABLE I

System.	$T_s$ (°C)	$T$ (°C)	$T_s - T$
IsoAmyl alcohol in glycerol	70-71°	64.3, 64.2, 64.6, 64.4	5-6
	58-59°	52.4, 53.0, 52.5	6-7
	51-52°	46.2, 46.4, 46.4	5-6
	40°	32.6, 32.3, ...	7-8
	35°	30.0, 30.2, ...	5
Phenol in hexane	42-43°	35.0, 36.0, 35.8	7-8
	39-40°	34.0, 35.0, 34.6	7-8
Aniline in hexane	58-60°	55.2, 55.6, 55.5	3-4
	53-54°	48.8, 48.0, 49.0	4-5
	52-53°	47.2, 47.0, 47.6	5-6
	44-45°	40.0, 40.6, 41.0	4-5
	41-42°	37.0, 37.6, 37.2	4-5
Water in ethyl acetate	65-66°	42.0, 41.0, 41.6	22-23
	60-61°	38.0, 37.0, 37.6	22-23
	50-51°	32.0, 31.8, 32.4	18-19
	40-41°	Did not separate down to room temperature	...
Glycerol in acetone	80-81°	69.8, 69.4, 69.6	10-11
	69-70°	62.0, 59.8, 60.0	8-9
	60-61°	52.0, 51.8, 52.0	8-9
	55-56°	46.0, 46.0, 47.0	9-10
	50-51°	42.0, 42.6, 42.0	8-9
	45-46°	36.0, 36.0, 35.8	8-9
	40-41°	Did not separate out at 32.4°	

Almost no supersaturation has been obtained in the following system:—

Aniline in water, water in aniline, nitrobenzene in water, phenol in water, *o*-nitrophenol in water, hexane in methyl alcohol, and methyl alcohol in hexane.

With this theoretical background in view the following experimental investigations were undertaken\*.

\* When the solubility becomes appreciably large, the simplifications made earlier would not be justified as the value of  $N_1V_1$  will be significant and hence the factor  $N_1V_1/N_1V_1+N_2V_2$ , of the original expression for solubility, cannot be put equal to unity. Under these circumstances Eq. 8) will take the form

$$T_s - T = \frac{2\sigma T_s}{I \left[ \frac{N_1V_1}{N_1V_1+N_2V_2} \right] r} = \frac{2\sigma T_s}{Ir} \left( 1 + \frac{N_1V_1}{N_2V_2} \right)^2$$

which denotes that even if all other conditions are identical, supersaturation will be greater, the higher the solubility.

The results given in Table I are summarised in Table II, which gives  $T_s - T$  along with  $\sigma$  in bulk and  $T_s - T$  calculated from eq. (8) for  $T_s = 300^\circ\text{K}$  for different systems. When proper values of different constant factors are substituted in (8), it simplifies to

$$T_s - T = \frac{2\sigma T_s}{I r} = \frac{\sigma}{9.88I} \quad (r = 1.5 \times 10^{-6} \text{ cm.}) \dagger\dagger$$

TABLE II

 $T_s = 300^\circ\text{K}$ 

System.	$\sigma$ in bulk.	$I$ †	$T_s - T$ (observed)	$T_s - T$ (calculated)
Aniline-water	5.7	0.86	Negligible	0.7
Nitrobenzene-water	23.9	1.28	"	1.9
Phenol-water	30.0*	0.97	"	3.1
o-Nitrophenol-water	30.0*	1.17	"	2.6
CS <sub>2</sub> -water	48.4**	1.52**	2**	4.0
Hexane-MeOH	4.4*	2.53	Negligible	0.2
Phenol-hexane	20.0*	0.89	5.6	2.3
isoAmyl alcohol-glycerol	24.0*	0.81	5.6	3.0
Acetone-glycerol ‡	40.0	(?)	8	...
Hexane-aniline	23.0	0.98	4.5	2.4
Water-ethyl acetate	6.0	3.54	18.0	0.2(?)

\* Calculated from Antonow's rule.

\*\* Cf. Davis (*loc.cit.*).

‡ Internal pressure not known.

† For internal pressures see Glasstone, "Recent Advances in General Chemistry", 1936, p. 265; also Mortimer (*J. Amer. Chem. Soc.*, 1923, **45**, 633).

From Table II it appears that the value of  $I$  is very nearly equal to unity in many cases. For such systems eq. (9) shows that  $T_s - T$  will be approximately proportional to  $\sigma$  as was conceived by Kenrick (*loc.cit.*). It may be seen from the last two columns of Table II that, although there is no exact correspondence between the calculated and the observed values of  $T_s - T$ , there is no doubt about the fact that these are very nearly similar in most of the cases. It is clear that systems like benzene-water, toluene-water, aniline-water, nitrobenzene-water and *vice versa*, hexane-methyl alcohol, methyl alcohol-hexane etc., will have negligible supersaturation ( $< 1^\circ$ ) as is corroborated by experimental evidence recorded in Table II. The apparent anomaly of ethyl acetate-water system can be accounted to be due to compound formation (Glasstone, "Recent

†† After Davis (*loc.cit.*). Frenkel ("Kinetic Theory of Liquids", 1946, p. 374) suggests  $r \approx 2 \times 10^{-6}$  cm. for nucleus droplet of water in stable equilibrium with water vapour at  $373^\circ\text{K}$ .

Advances in General Chemistry'', 1936, p. 258) and hence a large  $T_s - T$  results. In the case of phenol-water system, it is very probable that  $\sigma$  is not correctly given by Antonow's rule which holds only when the solubility is very low.

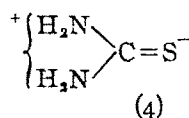
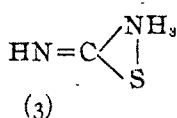
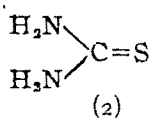
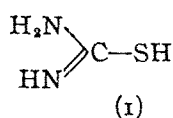
Table I shows clearly that supersaturation in liquid-liquid systems does exist, only we have to choose suitable systems for a clear manifestation *i.e.* systems with large  $\sigma$  and small  $I$ , as for example, systems like acetone-glycerol, phenol-hexane, isoamyl alcohol-glycerol, etc. Exact correspondence between calculated and observed  $T_s - T$  should not be expected, however, due to uncertainties in the value of ' $r$ ' even if  $\sigma$  and  $I$  are taken to be correctly known.

There is another remarkable fact which must be pointed out at this place. The cloud of separating solute (specially in cases of low solubility) appears almost simultaneously throughout the system. In other words, nucleus formation appears to occur throughout the systems almost at the same time, quite contrary to the mode of separation of the solid solute from a supersaturated solution. Besides, no stabilising effect of continued and prolonged heating has been observed in these systems. From what has been said above it is obvious that no heating effect is possible under these conditions of easy nucleus formation. It appears that as in liquid-liquid separation, no work is to be done for properly orientating the nucleus forming units into a lattice whose formation would involve a considerably larger amount of work than in the formation of a mere droplet of radius ' $r$ '. Hence, it is extremely easy for the solute molecules to form a nucleus as they move and meet their respective species. The difference in the internal pressures always tends to throw one out of the other, and hence the same molecular species will have a very strong tendency to go together in presence of another molecular species having a widely different internal pressure. Obviously, then, the supersaturation will be negligible in such cases as the difference in their internal pressures helps to reduce the necessary amount of work to be performed for nucleus formation. These reasons probably account for easy separating out of sparingly soluble liquids from their supersaturated solutions.

# A POTENTIOMETRIC STUDY OF THE CONSTITUTION OF THIOCARBAMIDE AND PHENYLTHIOCARBAMIDE

By R. D. GUPTA AND J. B. JHA

Various formulae have been proposed for thiocarbamide and its derivatives :



Potentiometric work embodied in this note establishes the acidic nature of the thiocarbamide and its derivatives in aqueous solution supporting partly the configuration (1).

A weak solution of phenylthiocarbamide was titrated potentiometrically with a weak solution of caustic soda.

The graphs (A) and (B) corresponding to the readings show two step-like bends. These correspond to two dissociation constants  $p_{k1}$  and  $p_{k2}$  : thiocarbamide 7.189, 7.381 ; phenylthiocarbamide 6.865, 7.189 establishing the dibasic nature of these substances.

Fig. 1  
(curve A)

Aq. phenylthiocarbamide soln. at 37°.

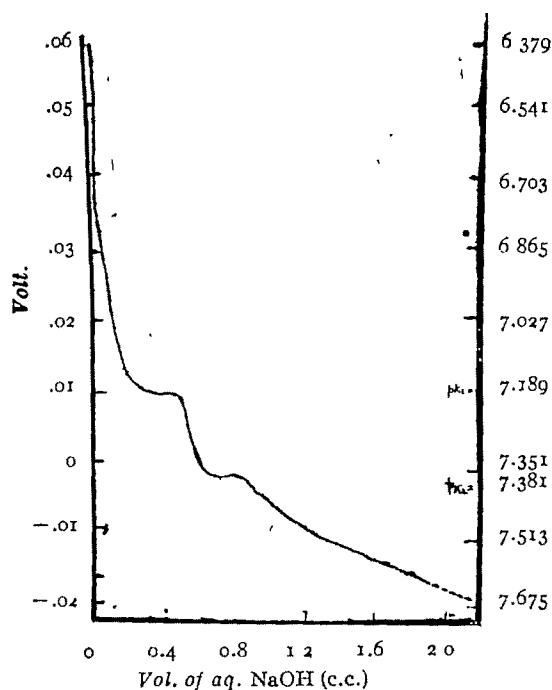
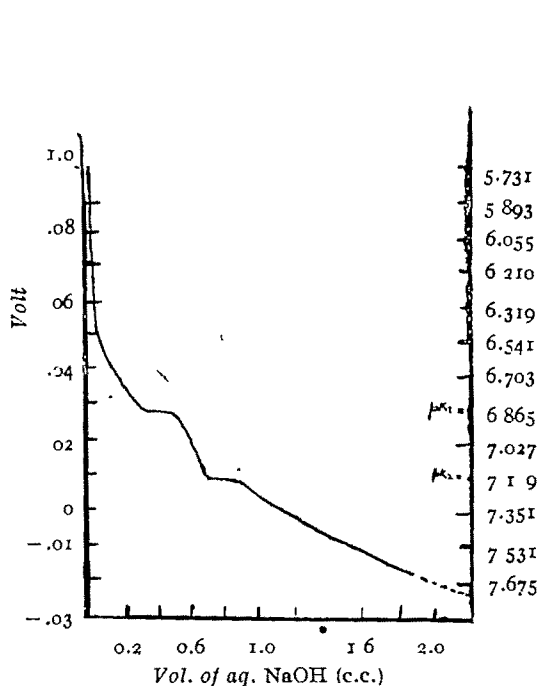


Fig. 2  
(curve B)

Aq. thiocarbamide soln. at 37°.





The titrations carried out in aqueous medium show that only 2% of the substance in each case are titratable, *i. e.* 98% are present in some other non-acidic form. Similar titrations in aqueous alcoholic solution resulted in the suppression of this acidity *i. e.* the disappearance of the step-like bends, already referred to.

This behaviour of thiocarbamide and its phenyl derivative opens up two possibilities, either (C), these substances are mixtures of two definite and separate forms or (D), the acidic and non-acidic forms are tautomers in equilibrium. Rejecting (C) it could be said with certainty that these compounds could not be separated into acidic and non-acidic forms. Further work is in progress to clarify the (D).

Part of the work was carried out in the Chemical laboratories, Agra College, with the kind permission and help of Dr. S. S. Deshapande.

BIRLA COLLEGE,  
PILANI, RAJASTHAN.

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# ON TITRATION OF SODIUM HYPONITRITE WITH MINERAL ACIDS

By T. M. OZA, N. L. DIPALI AND V. T. OZA

It is known that aqueous solutions of sodium hyponitrite decompose slowly into  $N_2O$  and  $NaOH$ , gradually in the cold, and rapidly when heated (cf. Divers, *J. Chem. Soc.*, 1899, 78, 95). Further, aqueous solutions of hyponitrous acid decompose into  $H_2O$  and  $N_2O$  rapidly at and above  $25^\circ$ , and slowly at  $0^\circ$  (cf. Hantzsch and Kauffmann, *Ber.*, 1896, 29, 317). It would therefore appear that decomposition of solutions of sodium hyponitrite may be the result of the hydrolysis of the salt into sodium hydroxide and hyponitrous acid. No nitrite or nitrate has been detected in the aqueous solutions (cf. Partington and Shah, *J. Chem. Soc.*, 1931, 2071). It thus appeared interesting if sodium hyponitrite could be determined simply by titrating its freshly made solution with a standard acid. The isosterism of carbon dioxide and nitrous oxide shows that sodium hyponitrite ( $Na_2O$ ,  $N_2O$ ) might behave like sodium carbonate ( $Na_2O$ ,  $CO_2$ ).

Sodium hyponitrite was prepared as by Oza (this *Journal*, 1944, 21, 71). It contained no nitrite or carbonate and on analysis it gave the following results: (i) 1.9082 g. (hydrated) gave 1.0322 g. on complete dehydration. The loss corresponds to 91.85 g. for  $Na_2N_2O_2$ ; (ii) 0.0119 g. (anhydrous substance) gave 0.0130 g.  $NaCl$  and 0.014 g. requires 5.85 c.c. of 0.04493N-KCNS (Oza and Walawalkar, *J. Indian Chem. Soc., Ind. & News Ed.*, 1946, 9, 57). (Found: Na, 43.1;  $N_2O_2$ %, 56.2. Calc. for  $Na_2N_2O_2$ : Na, 43.4;  $N_2O_2$ %, 56.6 per cent).

The results of titration at room temperature with 0.1N- $HNO_3$  are shown in Table I, while Table II contains results of similar experiments at the temperature of ice. Table III contains results of the experiments with 0.101N- $HCl$  in the ice-cold solution. In the experiments, a weighed quantity of the anhydrous salt is added to 20 c.c. of water and immediately titrated. When titrated in the ice-cold solution, ice-cold water is used and the flask is held in the ice cold bath. At room temperature, a deceptive end-point is witnessed with phenolphthalein, but this is not so at the temperature of ice when the titration reading is exactly half as much as with methyl orange. The cause of the deceptive end-point with phenolphthalein, at room temperature, may lie in the relative instability of the hydro-hyponitrite formed.

TABLE I

Titration of  $Na_2N_2O_2$  with standard  $HNO_3$  at room temperature

$Na_2N_2O_2$ taken.	Reading with 0.1013N- $HNO_3$ with		Percentage $Na_2N_2O_2$ found with	
	Phenolphthalein.	Methyl orange.	Phenolphthalein.	Methyl orange.
0.0222 g.	2.5 c.c.	4.25 c.c.	60.4	102.7
0.0338	3.7	6.3	58.7	100.0
0.0266	2.95	4.95	59.5	99.8
0.0342	3.80	6.45	59.6	101.1
0.0193	2.15	3.55	59.1	99.3

TABLE II

*Titration of  $\text{Na}_2\text{N}_2\text{O}_2$  with 0.1N- $\text{HNO}_3$  at 0°.*

$\text{Na}_2\text{N}_2\text{O}_2$ taken.	Reading with		Percentage $\text{Na}_2\text{N}_2\text{O}_2$ found with	
	Phenolphthalein.	Methyl orange.	Phenolphthalein	Methyl orange.
0.0286 g.	2.75 c.c.	5.5 c.c.	50.95	101.0
0.0226	2.15	4.3	50.42	100.8
0.0364	3.55	7.0	51.7	102.0
0.0346	3.30	6.55	50.55	100.3

TABLE III

*Titration of  $\text{Na}_2\text{N}_2\text{O}_2$  with 0.101N-  $\text{HCl}$  at 0°.*

$\text{Na}_2\text{N}_2\text{O}_2$ taken.	Reading with		Percentage $\text{Na}_2\text{N}_2\text{O}_2$ found with	
	Phenolphthalein.	Methyl orange.	Phenolphthalein.	Methyl orange.
0.0400 g.	3.9 c.c.	3.9 c.c.	51.2	102.4
0.0545	5.1	5.0	50.0	99.3

TABLE IV

*Titration of mixtures of  $\text{Na}_2\text{N}_2\text{O}_2$  and  $\text{NaOH}$  with 0.101N  $\text{HCl}$  at 0°.*

$\text{Na}_2\text{N}_2\text{O}_2$ taken.	Reading with		$\text{HCl}$ of $\text{NaOH}$ taken.	$\text{HCl}$ required with		$\text{Na}_2\text{N}_2\text{O}_2$ Calc.
	Phenolphthalein.	Methyl orange.		Phenolphthalein.	Methyl orange	
0.0101 g.	10.3 c.c.	0.95 c.c.	9.4 c.c.	0.90 c.c.	0.95 c.c.	0.0102 g.
0.0254	11.7	2.30	"	2.30	2.3	0.0253
0.0420	13.4	4.00	"	4.00	4.00	0.0424
0.0500	14.1	4.60	"	4.70	4.60	0.0499
0.0520	14.7	4.90	"	4.90	4.90	0.0524
0.0600	16.8	5.6	"	5.60	5.6	0.0599

The analogy between the carbonate and hyponitrite of sodium seems close for, mixtures of the hydroxide and hyponitrite could be titrated to determine the amounts of the two. The titration must be conducted at 0°. The results shown in Table IV have been obtained by titrating such mixtures, taking a measured volume of the hydroxide in a conical flask, cooling the solution and adding an accurately weighed quantity of the hyponitrite.

M. R. SCIENCE INSTITUTE,  
GUJARAT COLLEGE, AHMEDABAD  
AND  
KARNATAK COLLEGE, DHARWAR.

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# COMPLEX COMPOUNDS OF BIGUANIDE WITH BIVALENT METALS.

## PART XI. *p*-ACETYLAMINOPHENYLBIGUANIDE AND *p*-PHENYLENEBIGUANIDE COMPOUNDS OF COPPER, NICKEL AND CHROMIUM

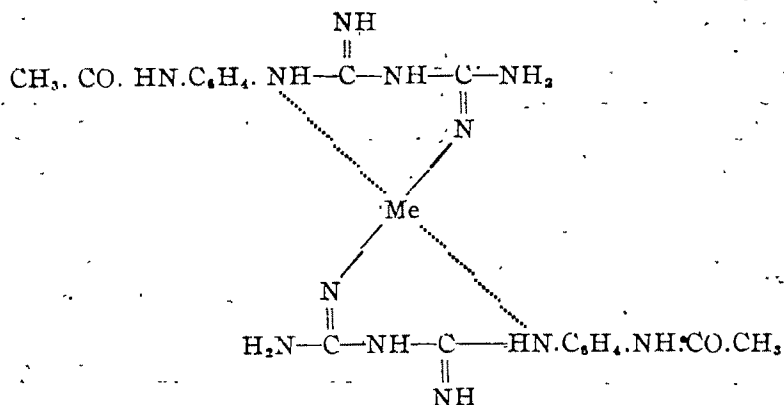
BY PRIYADARANJAN RÂY AND CHITTARANJAN GOUTAM

Complex compounds of *p*-acetylaminophenylbiguanide with bivalent copper and nickel have been prepared and their properties studied with a view to investigating the influence of substitution in the phenyl group on the nature of the complex formed. No complexes with trivalent chromium or cobalt could be isolated.

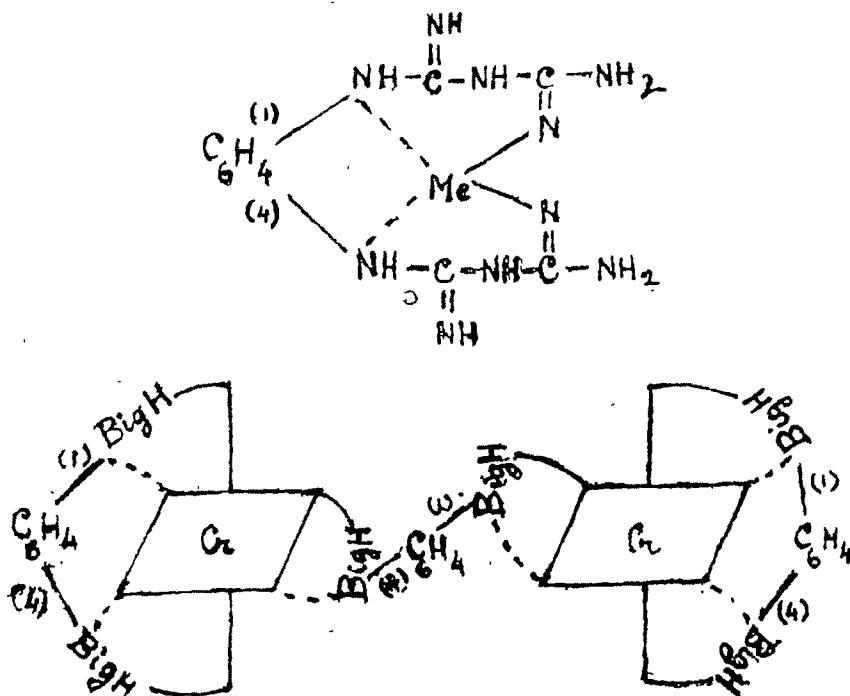
A study of the preparation and properties of the complex compounds of *p*-phenylenedibiguanide with bivalent copper and nickel shows that it resembles the *m*-phenylenedibiguanide in its behaviour in this respect, while it differs from the latter as it gives only a 6-coordinated dichromium tris-*p*-phenylenedibiguanide base.

The metallic complexes of both these reagents decompose more or less in boiling water, showing that substitution in the *para* position of the phenyl group in phenylbiguanide reduces the tendency to complex formation and the stability of the complexes.

Rây and Chakrabarty (this *Journal*, 1941, 18, 612) have described two modifications of copper phenylbiguanide complexes presumably related as *cis-trans* isomers, and three different modifications of nickel phenylbiguanidine. Three different varieties of nickel naphthylbiguanide base were also isolated by Rây and Ray (this *Journal*, 1944, 21, 163). It was therefore expected that *p*-acetylaminophenylbiguanide might also give rise to similar isomeric complexes with copper and nickel. This expectation was, however, not realised. None of the copper or nickel *p*-acetylaminophenylbiguanide complexes, described in the present paper, could, however, be obtained in more than one modification. Unlike phenylbiguanide, it has not also been possible to obtain any complex compounds of *p*-acetylaminophenylbiguanide with trivalent cobalt or chromium. The influence of substitution, giving rise probably to a steric effect, may account for this anomalous behaviour. The copper and nickel complexes may therefore be regarded to possess the *trans*-configuration as shown below:



*p*-Phenylenedibiguanide, which, like its *m*-phenylene analogue (cf. Rây and Siddhanta, *ibid.*, 1943, 20, 200; Rây and Das Sarma, *ibid.*, 1949, 26, 187), behaves as a quadridentate molecule, has been found to give as usual 4-coordinated copper and nickel complexes and only 6-coordinated dichromium tris-*p*-phenylenedibiguanide base. In this respect it differs from its *meta* isomer. The configuration of the 4- and 6-coordinated metallic complexes of this *para* derivative are represented below.



$C_6H_4(BigH_2)_2$  = a molecule of *p*-phenylenedibiguanide.

#### EXPERIMENTAL

*p*-Acetylaminophenylbiguanide Sulphate.—*p*-Aminoacetanilide (15g. in 80 c.c. water), dicyandiamide (8.4 g.) and 11c.c. of 32% HCl were heated together under reflux for half an hour. The hot, coloured solution was treated with 5 g. of animal charcoal and filtered. The filtrate was treated with a saturated solution of ammonium sulphate and rendered strongly acid with sulphuric acid. The sulphate of the biguanide base crystallised out from the solution. The crystals were purified by dissolving them in dilute ammonia, treating the hot solution with charcoal, and then acidifying the filtrate with sulphuric acid. For further purification, the product was dissolved in water and treated with ammoniacal copper sulphate solution. The complex copper acetylaminobiguanide sulphate was then decomposed with a moderately strong solution of sulphuric acid. The crystalline precipitate was washed free from copper sulphate and dissolved in caustic soda solution. On acidification with dilute sulphuric acid the pure *p*-acetylaminophenylbiguanide sulphate separated out. The crystalline product was filtered, washed first with water, then with alcohol, and finally dried in air. The substance is

sparingly soluble in water and reacts acidic to litmus. (Found: N, 24.67;  $\text{SO}_4$ , 28.16.  $\text{C}_{10}\text{N}_6\text{OH}_{14}\cdot\text{H}_2\text{SO}_4\cdot0.5\text{H}_2\text{O}$  requires N, 24.63;  $\text{SO}_4$ , 28.15 per cent).

*Copper bis-p-Acetylaminophenylbiguanide.*—When a solution of *p*-acetylaminophenylbiguanide sulphate in dilute ammonia was treated with an ammoniacal solution of copper sulphate, the sulphate of the copper complex was precipitated. This was filtered and thoroughly washed. From this complex sulphate the corresponding base was obtained by treatment with an excess of caustic soda solution. The orange coloured base was washed with water till free from sulphate. The product was dried in a desiccator over solid KOH.

The orange coloured base is somewhat soluble in water, but insoluble in alcohol. Its solution reacts alkaline to litmus and liberates ammonia from ammonium salts, m.p.  $206^\circ$  with decomposition. {Found: Cu, 11.69; N, 31.11;  $\text{H}_2\text{O}$  (by loss at  $110^\circ$ ), 1.66.  $[\text{Cu}(\text{C}_{10}\text{N}_6\text{OH}_{13})_2]$ ,  $0.5\text{H}_2\text{O}$  requires Cu, 11.79; N, 31.19;  $\text{H}_2\text{O}$ , 1.67 per cent}. [Found (for the dried product): Cu, 11.89; N, 31.70. Calc. Cu, 11.97; N, 31.70 per cent].

*The Complex Chloride.*—The above described complex copper base was digested, while still moist, with an excess of ammonium chloride solution on the water-bath till the evolution of ammonia ceased. The product was filtered and dissolved in water; and from the violet solution the complex chloride was precipitated by the addition of ammonium chloride. This was filtered, washed first with a little ice-cold water, then with alcohol, and finally dried in air.

The substance forms light violet crystals, soluble in water, m.p.  $204^\circ$  (decomp.). It also decomposes on boiling with water, giving a colloidal solution. {Found: Cu, 9.44; N, 25.03; Cl, 10.55;  $\text{H}_2\text{O}$  (by loss at  $110^\circ$ ), 10.65.  $[\text{Cu}(\text{C}_{10}\text{N}_6\text{H}_{14}\text{O})_2]$   $\text{Cl}_{2.4}\text{H}_2\text{O}$  requires Cu, 9.41; N, 25.05; Cl, 10.55;  $\text{H}_2\text{O}$ , 10.67 per cent}. {Found (for the dried product): Cu, 10.50; N, 27.78. Calc. Cu, 10.53; N, 27.88 per cent.}.

The *complex sulphate* was precipitated by adding an ammoniacal solution of copper sulphate to an ammoniacal solution of *p*-acetylaminophenylbiguanide sulphate. The rose-red precipitate was washed with water and dried in air. It is sparingly soluble in water, insoluble in alcohol, but soluble in hot dilute ammonia. {Found: Cu, 9.08; N, 23.93; S, 13.77;  $\text{H}_2\text{O}$  (by loss at  $110^\circ$ ), 10.28.  $[\text{Cu}(\text{C}_{10}\text{N}_6\text{H}_{14}\text{O})_2]\text{SO}_{4.4}\text{H}_2\text{O}$  requires Cu, 9.08; N, 24.03;  $\text{SO}_4$ , 13.72;  $\text{H}_2\text{O}$ , 10.29 per cent}. [Found (for the dried product): Cu, 10.10; N, 26.77. Calc. Cu, 10.11; N, 26.77 per cent].

*Nickel bis-p-acetylaminophenylbiguanide sulphate* was prepared by adding a solution of nickel sulphate to an ammoniacal solution of *p*-acetylaminophenylbiguanide sulphate. The brown precipitate was filtered, washed first with water, then with alcohol, and finally dried in air. The substance is sparingly soluble in water. {Found: Ni, 8.60; N, 24.98;  $\text{SO}_4$ , 14.16;  $\text{H}_2\text{O}$  (by loss at  $110^\circ$ ), 7.99.  $[\text{Ni}(\text{C}_{10}\text{N}_6\text{H}_{14}\text{O})_2]\text{SO}_{4.3}\text{H}_2\text{O}$  requires Ni, 8.67; N, 24.83;  $\text{SO}_4$ , 14.18;  $\text{H}_2\text{O}$ , 7.99 per cent}. [Found (for the dried product): Ni, 9.46; N, 27.19. Calc. Ni, 9.42; N, 27.01 per cent].

The *complex base* was obtained as a yellow product when the complex sulphate was triturated with an excess of alkali solution in a mortar. This was filtered, washed with water free from sulphate and then dried in a desiccator over solid KOH.

The substance is sparingly soluble in water and alcohol. Its solution is alkaline to litmus. It melts  $248^{\circ}$  with decomposition. It liberates ammonia from ammonium salt solution. {Found: Ni, 10.44; N, 29.95;  $\text{H}_2\text{O}$  (by loss at  $105^{\circ}$ ), 6.41.  $[\text{Ni}(\text{C}_{10}\text{N}_8\text{H}_{12}\text{O})_2] \cdot 2\text{H}_2\text{O}$  requires Ni, 10.47; N, 29.96;  $\text{H}_2\text{O}$ , 6.42 per cent}. [Found (for the dried product): Ni, 11.20; N, 31.98. Calc. Ni, 11.18; N, 31.98 per cent].

*The Complex Chloride.*—The complex base was converted into its chloride by digesting it with an excess of ammonium chloride solution on the water-bath. The brown product was filtered, washed first with water, then with alcohol, and afterwards dried in air. The substance is practically insoluble in water. {Found: Ni, 9.08; N, 25.70; Cl, 10.86;  $\text{H}_2\text{O}$  (by loss at  $110^{\circ}$ ), 8.29;  $[\text{Ni}(\text{C}_{10}\text{N}_8\text{H}_{11}\text{O})_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  requires Ni, 9.01; N, 25.78; Cl, 10.89;  $\text{H}_2\text{O}$ , 8.28 per cent}. [Found (for the dried product): Ni, 9.85; N, 28.16. Calc. Ni, 9.82; N, 28.10 per cent].

All attempts to prepare the corresponding complexes with trivalent cobalt and chromium ended in failures.

*p-Phenylenedibiguanide Sulphate.*—*p*-Phenylenediamine (10 g.), dicyandiamide (17 g.), 22 c.c. of 32% hydrochloric acid and 25 c.c. of water were heated under reflux for about 2 hours. To the cold mixture, 100 c.c. of alcohol were added. The solution was then boiled with 5 g. of charcoal for a few minutes. The cold filtrate was then treated with 30 c.c. of dilute sulphuric acid (1:2 by volume). The crystals of the sulphate were filtered, washed first with cold water and then with alcohol and dried in air. (Found: N, 37.60;  $\text{SO}_4$ , 25.71.  $\text{C}_{10}\text{N}_{10}\text{H}_{18} \cdot 2\text{H}_2\text{SO}_4$  requires N, 37.43;  $\text{SO}_4$ , 25.66 per cent).

*Copper p-phenylenedibiguanidinium sulphate* was obtained as a violet coloured powder by adding an ammoniacal solution of *p*-phenylenedibiguanide sulphate to an ammoniacal solution of copper sulphate. The product was filtered, washed and dried as usual. It is very sparingly soluble in water. {Found: Cu, 13.20; N, 28.89;  $\text{SO}_4$ , 19.90;  $\text{H}_2\text{O}$  (by loss at  $105^{\circ}$ ), 9.37.  $[\text{Cu}(\text{C}_{10}\text{N}_{10}\text{H}_{18})]\text{SO}_4 \cdot 2.5\text{H}_2\text{O}$  requires Cu, 13.20; N, 29.10;  $\text{SO}_4$ , 19.97;  $\text{H}_2\text{O}$ , 9.36 per cent}. Found (for the dried product): Cu, 14.54; N, 31.90. Calc. Cu, 14.47; N, 32.10 per cent.

The complex base was obtained from the above described complex sulphate when the latter, while still moist, was triturated with an excess of caustic soda solution in a mortar. The product was washed first with water till free from sulphate, then with alcohol, and finally dried in a desiccator over solid KOH.

It forms a pale violet powder, insoluble in cold water and organic solvents. The substance slowly absorbs  $\text{CO}_2$  from air and liberates ammonia from solutions of ammonium salts. {Found: Cu, 12.88; N, 28.38;  $\text{H}_2\text{O}$  (by loss at  $105^{\circ}$ ), 31.10.  $[\text{Cu}(\text{C}_{10}\text{N}_{10}\text{H}_{14})] \cdot 8.5\text{H}_2\text{O}$  requires Cu, 12.94; N, 28.53;  $\text{H}_2\text{O}$ , 31.19 per cent}. [Found (for the dried product): Cu, 18.80; N, 41.10. Calc. Cu, 18.81; N, 41.48 per cent].

The complex chloride was obtained by digesting the complex base with ammonium chloride solution on the water-bath till the evolution of ammonia ceased. The product was filtered, washed and dried as usual.

The substance forms light violet powder, insoluble in cold water. {Found: Cu, 13.70; N, 29.83; Cl, 15.36;  $\text{H}_2\text{O}$  (by loss at  $105^{\circ}$ ), 11.58.  $[\text{Cu}(\text{C}_{10}\text{N}_{10}\text{H}_{18})]\text{Cl} \cdot 3\text{H}_2\text{O}$

requires Cu, 13.66; N, 30.01; Cl, 15.28, H<sub>2</sub>O, 11.62 per cent}. [Found (for the dried product): Cu, 14.99; N, 34.20; Cl, 17.05. Calc. Cu, 15.07; N, 34.10; Cl, 17.10 per cent].

*Nickel p-phenylenedibiguanidinium sulphate* was obtained as a brick-red flocculent precipitate when an ammoniacal solution of *p*-phenylenedibiguanide sulphate was treated with that of nickel sulphate. This was washed and dried as usual. The substance is very sparingly soluble in hot water, but insoluble in alcohol. {Found: Ni, 12.50; N, 29.84; SO<sub>4</sub>, 20.50; H<sub>2</sub>O (by loss at 105°), 7.68. [Ni(C<sub>10</sub>N<sub>10</sub>H<sub>16</sub>)]SO<sub>4</sub>·2H<sub>2</sub>O requires Ni, 12.57; N, 29.98; SO<sub>4</sub>, 20.50; H<sub>2</sub>O, 7.70 per cent}. [Found (for the dried substance): Ni, 13.58; N, 32.39; SO<sub>4</sub>, 22.29. Calc. Ni, 13.62; N, 32.50; SO<sub>4</sub>, 22.30 per cent].

The *complex base* was prepared by triturating the above described complex sulphate, while still moist, with an excess of caustic soda solution in a mortar. The dull red insoluble product was washed with water till free from sulphate and then dried over solid KOH in a desiccator. It gives alkaline reaction, absorbs CO<sub>2</sub> from air, and liberates ammonia from ammonium salt solutions. {Found: Ni, 14.87; N, 35.43; H<sub>2</sub>O (by loss at 105°), 15.95. [Ni(C<sub>10</sub>N<sub>10</sub>H<sub>14</sub>)]·3.5H<sub>2</sub>O requires Ni, 14.90; N, 35.55; H<sub>2</sub>O, 15.92 per cent}. [Found (for the dried product): Ni, 17.60; N, 41.84. Calc. Ni, 17.53; N, 41.82 per cent].

*The Complex Chloride.*—The chloride of the complex base was obtained by digesting the base with an excess of ammonium chloride solution on the water-bath till the evolution of ammonia ceased. The insoluble, dull red product was filtered, washed and dried as usual. {Found: Ni, 12.66; N, 30.33; Cl, 15.40; H<sub>2</sub>O (by loss at 110°), 11.70. [Ni(C<sub>10</sub>N<sub>10</sub>H<sub>14</sub>)]Cl<sub>2</sub>·3H<sub>2</sub>O requires Ni, 12.76; N, 30.46; Cl, 15.40; H<sub>2</sub>O, 11.74 per cent}. [Found (anhydrous product): Ni, 14.40; N, 33.59; Cl, 17.45. Calc. Ni, 14.46; N, 33.60; Cl, 17.50 per cent].

*Chromium tris-p-Phenylenedibiguanide Base.*—The complex chromium base was obtained as a rose-red precipitate by adding a solution of chrome alum to that of *p*-phenylenedibiguanide sulphate in caustic soda. The product was washed with ice-cold water till free from sulphate, then with alcohol, and afterwards dried over solid KOH in a desiccator. The substance is moderately soluble in water and reacts alkaline to litmus. It liberates ammonia from ammonium salt solutions. {Found: Cr, 10.15; N, 40.96; H<sub>2</sub>O (by loss at 105°), 6.33. [Cr<sub>2</sub>(C<sub>10</sub>N<sub>10</sub>H<sub>14</sub>)<sub>3</sub>]·5H<sub>2</sub>O requires Cr, 10.17; N, 41.09; H<sub>2</sub>O, 8.85 per cent}. [Found (dried at 105°): Cr, 11.04; N, 44.32. [Cr<sub>2</sub>(C<sub>10</sub>N<sub>10</sub>H<sub>14</sub>)<sub>3</sub>]·1.5H<sub>2</sub>O requires Cr, 11.03; N, 44.53 per cent}.

No salt of the complex chromium base could, however, be isolated. Similarly all attempts to prepare cobalt tris-*p*-phenylenedibiguanide complexes led to no fruitful results.

All the metallic complexes of *p*-acetylaminophenylbiguanide, as well as of *p*-phenylenedibiguanide, described here, decompose with boiling water. It therefore appears that substitution in the *para* position of the phenyl group in phenylbiguanide reduces the tendency to complex formation and the stability of the complex.



## STUDIES ON FERRI-PHOSPHORIC ACID COMPLEXES

By SUKUMAR BANERJEE

Ferri-phosphoric acid system has been studied in solution by different physico-chemical methods. Two complex ions have been detected and formulated as  $\text{Fe}(\text{HPO}_4)^+$  and  $\text{Fe}(\text{HPO}_4)_2^-$ .

Ferric iron forms complex ions with phosphoric acid as is shown by the disappearance of colour, lowering of oxidation potential, inability to liberate iodine from potassium iodide, etc. The use of phosphoric acid to convert ferric ion into a complex is also well known, but the number of complex ions formed and their nature have not been definitely established. Ritca and Meduri (*Gazzetta*, 1934, **64**, 235) from conductometric measurements of ferric chloride-phosphoric acid mixtures have obtained a maxima at 1:1, and have formulated the compound as  $\text{H}_3[\text{Cl}_3\text{FePO}_4]$ , but Jensen (*Z. anorg. Chem.*, 1934, **221**, 1) has shown that the complex formed is purely a phosphato complex and not a mixed chloro-phosphato complex. The same compound has also been detected by Lanford and Samuel (*J. Amer. Chem. Soc.*, 1942, **64**, 291) by applying Job's method of continued variation in ferric nitrate-phosphoric acid mixtures employing thiocyanate solution for colorimetric determination of ferric ion. The formula of the imperfect complex has been established as  $\text{Fe}(\text{HPO}_4)^+$ ; and from the study of the equilibrium the same workers have determined the dissociation constant of the complex ion using thiocyanate as the indicator for free ferric ion.

Babko and Kodenskaya (*Compt. rend. Acad. Sci. U.S.S.R.*, 1946, **52**, 37; *J. Gen. Chem. U.S.S.R.*, 1946, **16**, 1549; 1947, **17**, 1080) as also Chatterjee (*Science & Culture*, 1949, **15**, 201) have shown that in ferric-thiocyanate system in aqueous solution there is a dynamic equilibrium between the reactant ions and as many as five different complex ions:  $\text{Fe}(\text{SCN})^{++}$ ,  $\text{Fe}(\text{SCN})_2^+$ ,  $\text{Fe}(\text{SCN})_3$ ,  $\text{Fe}(\text{SCN})_4^-$  and  $\text{Fe}(\text{SCN})_5^{--}$ , the formation of which will disturb the equilibrium between ferric ion and phosphoric acid when thiocyanate is used for the determination of free ferric ion in equilibrium. Moreover, the measured intensity of the red colour formed is due to the total contribution of all the five ferri-thiocyanate complexes, the individual contributions of each of which are not known. But the individual concentrations of these ferri-thiocyanate complexes will vary with the varying concentration of the reactants which actually happens in the case under consideration. Further, the colour gradually fades away with time, and hence, the use of thiocyanate for the determination of the concentration of free ferric ion in equilibrium cannot be recommended. In the present investigation attempts have been made to study the ferri-phosphoric acid system by different physico-chemical methods such as thermometric, conductometric, colorimetric and modified transport experiments to detect the complex ions formed. Two phosphato complexes have been detected, containing ferric: phosphate in the ratio of 1:1 and 1:2, which have been formulated as  $\text{Fe}(\text{HPO}_4)^+$  and  $\text{Fe}(\text{HPO}_4)_2^-$ .

## E X P E R I M E N T A L

The stock solutions were prepared by dissolving AnalaR quality ferric chloride and phosphoric acid in water. The ferric chloride solution was standardised against dichromate using diphenylamine as an indicator, and the phosphoric acid solution standardised against alkali using a mixture of two parts of phenolphthalein and one part of  $\alpha$ -naphtholphthalein ( $p_n$  9.6) as the indicator.

*Thermometric Titration*

The arrangement for the thermometric titration is the same as has been previously described by Halder (this *Journal*, 1946, 23, 157). Both phosphoric acid and ferric chloride were alternately used as the titre.

TABLE I

Conc. of  $\text{FeCl}_3$  soln. = 1 M. Conc. of  $\text{H}_3\text{PO}_4$  soln. = 5M.  
 $\text{FeCl}_3$  taken = 40 c.c. (cf. Fig. 1).

$\text{H}_3\text{PO}_4$ added.	Temp.	Total rise in temp.	$\text{H}_3\text{PO}_4$ added	Temp.	Total rise in temp.	$\text{H}_3\text{PO}_4$ added	Temp.	Total rise in temp.
0 c.c.	3.190°	0.000	7 c.c.	1.675°	1.515	13 c.c.	1.200°	1.990
1	2.950°	0.240	8	1.540°	1.650	14	1.180°	2.010
2	2.695°	0.495	9	1.425°	1.765	15	1.175°	2.015
3	2.450°	0.740	10	1.345°	1.845	16	1.175°	2.015
4	2.225°	0.965	11	1.280°	1.910	17	1.175°	2.015
5	2.025°	1.165	12	1.230°	1.960	18	1.175°	2.015
6	1.840°	1.350				19	1.175°	2.015

TABLE II

Conc. of  $\text{FeCl}_3$  soln. = 0.5M. Conc. of  $\text{H}_3\text{PO}_4$  soln. = 2.5M.  
 $\text{FeCl}_3$  taken = 40 c.c. (cf. Fig. 2).

$\text{H}_3\text{PO}_4$ added.	Temp.	Total rise in temp.	$\text{H}_3\text{PO}_4$ added.	Temp.	Total rise in temp.	$\text{H}_3\text{PO}_4$ added.	Temp.	Total rise in temp.
0 c.c.	4.875°	0.000°	7 c.c.	4.360°	0.515°	13 c.c.	4.215°	0.660°
1	4.805	0.070	8	4.315	0.560	14	4.210	0.665
2	4.725	0.150	9	4.280	0.595	15	4.205	0.670
3	4.640	0.235	10	4.250	0.625	16	4.200	0.675
4	4.560	0.315	11	4.235	0.640	17	4.200	0.675
5	4.480	0.395	12	4.225	0.650	18	4.200	0.675
6	4.420	0.455				19	4.200	0.675

TABLE III

Conc. of  $\text{FeCl}_3$  soln. = 0.5M. Conc. of  $\text{H}_3\text{PO}_4$  soln. = 5M. $\text{FeCl}_3$  taken = 40 c.c. (Fig. 3)

$\text{H}_3\text{PO}_4$ added.	Temp.	Total rise in temp.	$\text{H}_3\text{PO}_4$ added.	Temp.	Total rise in temp.	$\text{H}_3\text{PO}_4$ added.	Temp.	Total rise in temp.
0 c.c.	3.330°	0.000°	4 c.c.	2.400°	0.930°	8 c.c.	2.050	1.280°
0.5	3.215	0.115	4.5	2.320	1.010	8.5	2.025	1.305
1	3.080	0.250	5	2.260	1.070	9	2.000	1.330
1.5	2.945	0.385	5.5	2.205	1.125	9.5	1.980	1.350
2	2.810	0.520	6	2.165	1.165	10	1.960	1.370
2.5	2.700	0.630	6.5	2.130	1.200	10.5	1.940	1.390
3	2.580	0.750	7	2.100	1.230	11	1.920	1.410
3.5	2.485	0.845	7.5	2.070	1.260			

TABLE IV

Conc. of  $\text{FeCl}_3$  soln. = 2M. Conc. of  $\text{H}_3\text{PO}_4$  soln. = 1M. $\text{H}_3\text{PO}_4$  taken = 40 c.c. (Fig. 4).

$\text{FeCl}_3$ added.	Temp.	Total rise in temp.	$\text{FeCl}_3$ added.	Temp.	Total rise in temp.	$\text{FeCl}_3$ added.	Temp.	Total rise in temp.
0 c.c.	4.170°	0.000°	9 c.c.	2.410°	1.760°	17 c.c.	1.520°	2.650°
1	3.970	0.200	10	2.250	1.920	18	1.460	2.710
2	3.745	0.425	11	2.110	2.060	19	1.415	2.755
3	3.520	0.650	12	1.980	2.190	20	1.370	2.800
4	3.310	0.860	13	1.875	2.295	21	1.330	2.840
5	3.110	1.060	14	1.770	2.400	22	1.295	2.875
6	2.920	1.250	15	1.670	2.500	23	1.265	2.905
7	2.740	1.430	16	1.590	2.580	24	1.235	2.935
8	2.570	1.600						

*Conductometric Methods*

A dilute solution of ferric chloride was titrated conductometrically against a concentrated solution of phosphoric acid. In the arrangement for the determination of conductivity the principle of Wheatstone bridge was employed. The alternate current was supplied by a valve oscillator of the Hartley type giving an accurately determined frequency, free from harmonics. The sharpness of the minima was enhanced by a vacuum tube amplifier, the telephone being connected to the plate-circuit of the vacuum tube. Solutions for all conductivity experiments were prepared in twice distilled water and the conductivity cell was kept in an electrically controlled thermostat.

Conductivity measurements were also carried out in various solutions of ferric chloride, phosphoric acid and equimolecular mixtures of ferric chloride and phosphoric

acid to determine the formula of the complex formed by employing Job's method (*Ann. chim.*, 1928, x, 9, 113) of continued variation. The difference in the conductivity of the mixture from the additive conductivity of the individual reactants was plotted to get the composition corresponding to the maximum complex formation.

TABLE V

Conc. of  $\text{FeCl}_3$  soln. = 0.01M. Conc. of  $\text{H}_3\text{PO}_4$  soln. = 1.2832M.  
 $\text{FeCl}_3$  taken = 50 c.c. Temp. =  $27 \pm 0.1$ . (Fig 5).

$\text{H}_3\text{PO}_4$ added (c.c.)	0.00	0.12	0.24	0.36	0.48	0.60	0.72	0.84	0.96	1.08	1.20	1.32	1.44
$\frac{1}{R} \times 10^3$ (mhos)	11.11	16.03	21.74	26.53	28.57	30.21	31.35	31.95	33.00	33.44	33.90	34.84	35.46

TABLE VI

*Conductometric measurements.*

Conc. of  $\text{FeCl}_3$  soln. = 0.04M. Conc. of  $\text{H}_3\text{PO}_4$  soln. = 0.04M. Temp. =  $27 \pm 0.1^\circ$ . (Fig. 6).

Conductivity of $\text{H}_3\text{PO}_4$ .			Conductivity of $\text{FeCl}_3$ .			Conductivity of the mixture.			Difference. $[1/R_3 - (1/R_1 + 1/R_2)]$ $\times 10^3$ .
$\text{H}_3\text{PO}_4$ . 10 c.c.	Water. $1/R_1 \times 10^3$ .		$\text{FeCl}_3$ . 90 c.c.	Water. $1/R_2 \times 10^3$ .		$\text{H}_3\text{PO}_4$ . 10 c.c.	$\text{FeCl}_3$ . 90 c.c.		
20	80	6.48	20	20	139.86	20	80	155.04	8.70
30	70	10.85	30	30	133.33	30	70	158.73	14.55
40	60	14.54	40	40	125.00	40	60	161.29	21.75
50	50	17.63	50	50	99.01	50	50	158.73	42.09
53	47	20.53	53	53	83.68	53	53	153.85	49.64
56	44	21.05	56	56	80.65	56	47	149.25	47.55
60	40	21.86	60	60	75.19	60	44	142.86	45.31
63	37	22.86	63	63	69.44	63	40	133.33	41.03
65	35	23.72	65	65	64.52	65	37	126.58	38.34
67	33	24.27	67	67	61.73	67	35	120.48	34.48
70	30	24.66	70	70	58.82	70	33	115.61	32.13
72	28	25.22	72	72	54.64	72	30	107.53	27.67
74	25	25.91	74	74	51.02	74	28	102.04	25.11
75	20	26.46	75	75	46.30	75	25	93.90	21.14
80	20	27.86	80	80	38.46	80	20	80.00	13.68
90	10	30.03	90	90	21.14	90	10	54.05	2.88

*Colorimetric Titration*

The colour of the free ferric ion is a suitable property to follow the progress of the reaction by colorimetric titration, as the colour gradually disappears with the addition of phosphoric acid. The percentage of light transmitted through ferric chloride solution was measured with Lumetron Photoelectric colorimeter, model 400G, of Photovolt Corporation, New York; and then the percentage readings were converted into optical density. The arrangement and the method of measurements are the same as has been described in a previous paper of the author (Haldar and Banerjee, *Proc. Nat. Inst. Sci. India*, 1948, 14, 1). Distilled water was used as the standard and measurements were taken at wave-length of 490 m $\mu$ .

TABLE VII

Conc. of  $\text{FeCl}_3$  soln. = 0.1M. Conc. of  $\text{H}_3\text{PO}_4$  soln. = 5M.  $\text{FeCl}_3$  taken = 20 c.c.

$\text{H}_3\text{PO}_4$ added.	Opt. $D \times 10^3$ .	$\text{H}_3\text{PO}_4$ added.	Opt. $D \times 10^3$ .	$\text{H}_3\text{PO}_4$ added.	Opt. $D \times 10^3$ .
0.00 c.c.	80.97	0.25 c.c.	35.65	0.50 c.c.	16.75
0.05	63.83	0.30	31.88	0.55	14.27
0.10	53.76	0.35	27.57	0.60	11.35
0.15	46.85	0.40	23.46	0.65	9.96
0.20	42.02	0.45	20.07	0.70	8.35

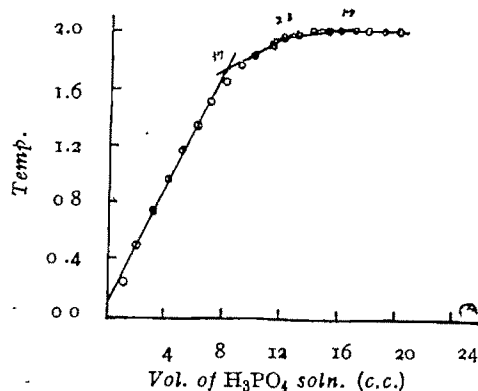
### Transport Experiments

Transport experiments were carried out to determine the nature of the charge of the complexes formed. The transport apparatus used is due to Clement and Duval (*Bull. soc. chim.*, 1938, v, 5, 1020). The base of the apparatus was filled with a mixture containing ferric chloride and excess of phosphoric acid. The limbs above the stoppers were filled with potassium chloride solution and connected to a source of 105 volts D.C., through platinum wires, and electrolysed for half-an-hour. The potassium chloride solution from the anode compartment, when tested with potassium ferrocyanide, gave definite indication of ferric radical. The experiment was again repeated with a mixture of ferric chloride and phosphoric acid in the ratio of 1:1; and the solution from the cathode compartment, when tested with ammonium molybdate, indicated the presence of phosphate. Blank experiments were carried out in each case under identical conditions but without passing electric current and the solutions from the anode and the cathode compartments were found free from ferric and phosphate radicals.

### DISCUSSION

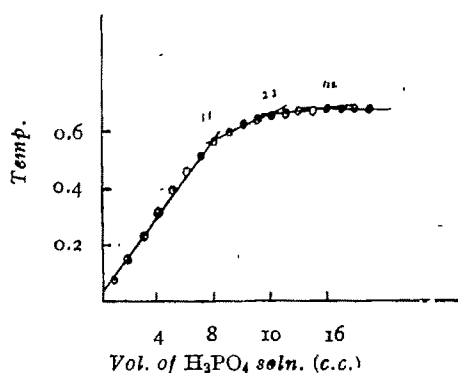
In the thermometric titration curves (Figs. 1, 2 and 3) obtained by direct titrations, three breaks appear at the points corresponding to ferric chloride: phosphoric acid

FIG. 1



[Table I: M- $\text{FeCl}_3$  and 5M- $\text{H}_3\text{PO}_4$ ]

FIG. 2



[Table II: 0.5 M- $\text{FeCl}_3$  and 2.5 M- $\text{H}_3\text{PO}_4$ ]

FIG. 3

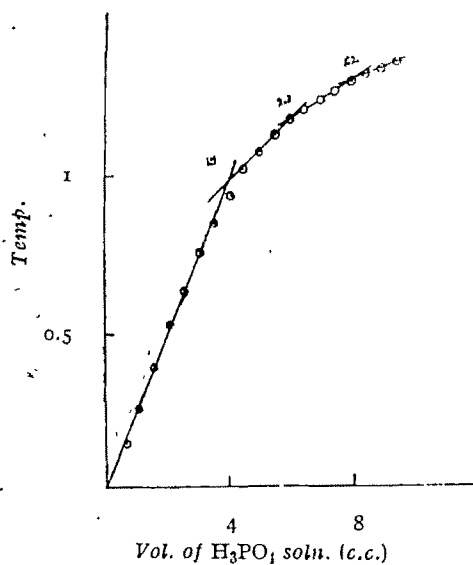
[Table III: 0.5 M-FeCl<sub>3</sub> and 5M-H<sub>3</sub>PO<sub>4</sub>]

FIG. 4

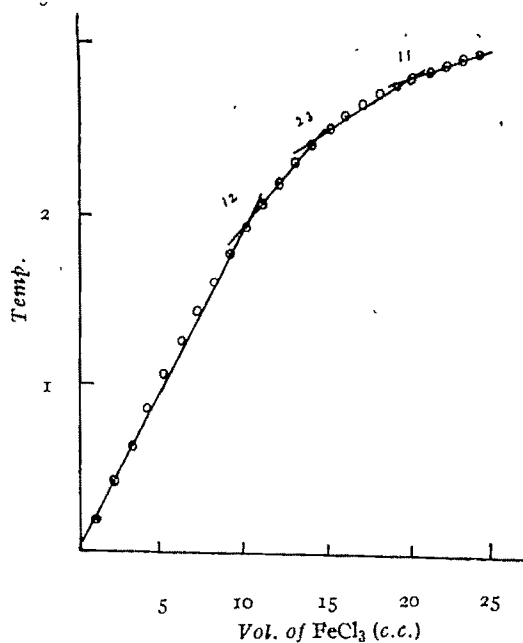
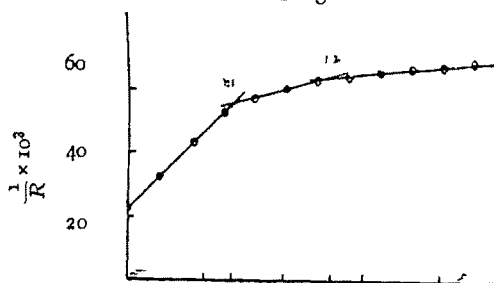
[Table IV: 2M-FeCl<sub>3</sub> and M-H<sub>3</sub>PO<sub>4</sub>]

FIG. 5



25 32.5 50 65 75 100  
Drops of H<sub>3</sub>PO<sub>4</sub> → 100 drops of H<sub>3</sub>PO<sub>4</sub> = 1.2 c.

[Table V: 0.01M-FeCl<sub>3</sub> and 1.2832M-H<sub>3</sub>PO<sub>4</sub>]

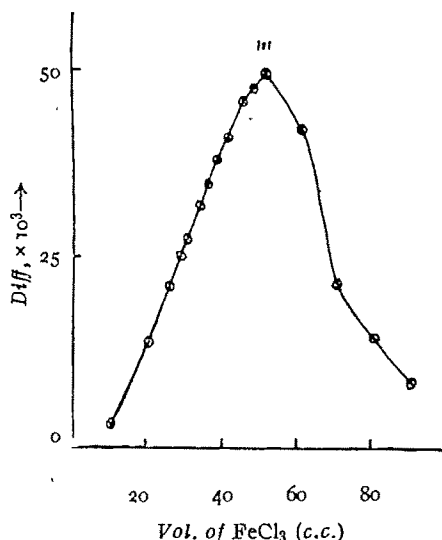
in the ratio of 1 : 1, 2 : 3 and 1 : 2. The break corresponding to Fe<sup>+++</sup> : H<sub>3</sub>PO<sub>4</sub> = 2 : 3 may be due to a mixture of 1 : 1 and 1 : 2 and so may not represent a new compound formation. The curve (Fig. 4) in the reverse titration, i.e., when ferric chloride has been used as the titre shows all the breaks as in the direct titrations.

The conductometric titration curve (Fig. 5) shows two breaks at ferric : phosphate = 1 : 1 and 1 : 2, confirming the results of thermometric titrations. In this curve no break corresponding to the compound ferric : phosphate = 2 : 3 is observed and so the breaks in the thermometric titration curves corresponding to this point do not represent true compound formation.

In the Job's method of continued variation, when the difference in conductivity is plotted against the volume of ferric chloride, a sharp maxima is obtained (Fig. 6) at

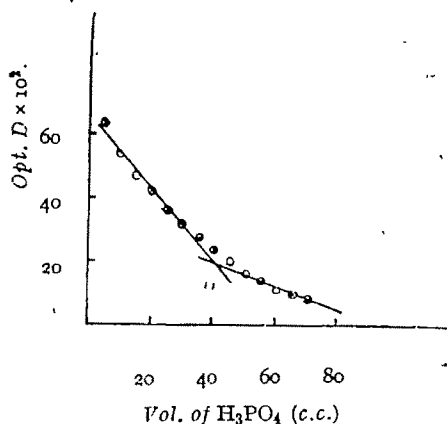
50 c.c. of ferric chloride corresponding to the point ferric : phosphoric acid equal to 1 : 1, but there is no indication of the other compound containing ferric and phosphoric

FIG. 6



[Table VI: 0.04 M-FeCl<sub>3</sub>+0.04 M-H<sub>3</sub>PO<sub>4</sub>]

FIG. 7



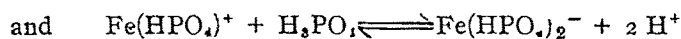
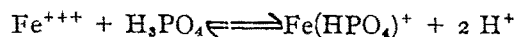
[Table VII: 0.1 M-FeCl<sub>3</sub>+5M-H<sub>3</sub>PO<sub>4</sub>]

acid in the ratio of 1 : 2. It has been shown by Job himself that in the case of more than one compound formation, indications are obtained for all the compounds only under the most favourable conditions. The colorimetric titration curve (Fig. 7) also shows a sharp break at the point 1 : 1 excluding the first point.

Thus, the compounds containing ferric : phosphoric acid = 1 : 1 and 1 : 2 are indicated by various methods within the range of 0.01M to 1M solutions of ferric chloride and are therefore sufficiently established.

The presence of phosphate radical in the cathode compartment in the 1 : 1 mixture of ferric chloride and phosphoric acid, as shown by the transport experiment, indicates that the phosphato complex of the above composition is positively charged, and hence, may be formulated as  $\text{Fe}(\text{HPO}_4)^+$ . This is in agreement with the formulation suggested by Lanford and Samuel (*loc. cit.*). The formulation as chloro-phosphato complex  $\text{H}_3[\text{Cl}_3\text{FePO}_4]$  by Ricca and Meduri (*loc. cit.*) cannot explain the presence of phosphate radical in the cathode compartment, and is therefore untenable. On the same basis the other complex ion containing ferric : phosphoric acid in the ratio of 1 : 2 may be formulated as  $\text{Fe}(\text{HPO}_4)_2^-$ , which indicates that iron should migrate to the anode during transport experiment and is actually found to be so. If the number of hydrogen atoms in the complex forming phosphate radical be assumed to be other than one, the nature of the charge of the complex ions will be changed, and the assumption cannot explain the results of the transport experiment. If, for example, the complex forming phosphato radical be  $(\text{H}_2\text{PO}_4)^-$  the complex ions will be  $\text{Fe}(\text{H}_2\text{PO}_4)^{++}$  and  $\text{Fe}(\text{H}_2\text{PO}_4)_2^+$ , in which case the presence of iron in anode compartment cannot be explained.

Thus, in a solution containing excess of phosphoric acid and ferric ion, two complex ions,  $\text{Fe}(\text{HPO}_4)^+$  and  $\text{Fe}(\text{HPO}_4)_2^-$  are formed according to the reactions :



The author's best thanks are due to Prof. P. B. Sarkar, Dr.es.Sc., F.N.I., Ghosh Professor of Chemistry and Dr. B. C. Halder, D.Phil., Asst. Lecturer in Chemistry of the Calcutta University for their keen interest, helpful suggestions and all laboratory facilities during the progress of the work.

GHOSH PROFESSOR'S CHEMISTRY LABORATORY,  
UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA.

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## PHOTONITRIFICATION AND NITROGEN LOSS FROM SOLUTIONS OF DIFFERENT AMMONIUM SALTS

BY N. R. DHAR AND M. C. PANT

Nitrification of several ammonium salts has been carried out in sunlight and in dark. The effect of sunlight has been found in all cases to accelerate nitrification.

The process of nitrification is always associated with the loss of nitrogen through the intermediate formation of ammonium nitrite.

In publications from this laboratory, it has been emphasised that light plays an important rôle in many oxidation reactions and the process of ammonification, nitrification and loss of nitrogen are markedly accelerated by light absorption.

We have carried on further experiments on nitrification of numerous ammonium salt solutions in sunlight and in the dark and our results are recorded in this paper.

### E X P E R I M E N T A L

Different ammonium salt solutions (100 c.c. each) were taken in conical glass flasks. In each case the nitrogen content at the beginning of the experiments was kept at 0.4, 0.2, 0.1 and 0.05 g. nitrogen per 100 c.c. of solution. Precipitated calcium carbonate (1 g.) was added to each flask to serve as a surface. Each solution was taken in two sets of flasks, one set was exposed to sunlight and the other was kept covered with black cloth to exclude light radiations by the side of the exposed sets.

After an exposure of five to six weeks the contents of the flasks were analysed for ammoniacal nitrogen left unoxidised and the nitric nitrogen formed due to the oxidation of ammonium salts by the usual methods.

The experimental results are recorded below.

TABLE I

#### I. Ammonium persulphate solutions exposed from 10-12-1946 to 10-1-47. (Mean temp. = 32°).

No.	Original N per 100 c.c. soln.	NH <sub>3</sub> -N left un- oxidised in		Nitric N formed in		Loss of N in	
		Light.	Dark.	Light.	Dark.	Light.	Dark.
1	0.40 g.	0.3681 g.	0.3814 g.	0.0241 g.	0.0179 g.	2.0%	0.3%
2	0.20	0.1231	0.1318	0.0144	0.0099	31.4	29.4
3	0.10	0.0714	0.0779	0.0048	0.0018	23.8	20.3
4	0.05	0.0298	0.0323	0.0021	0.0012	36.2	33.0

#### II. Ammonium sulphate solutions exposed from 21-1-47 to 7-3-47. (Mean temp. = 35.5°).

		Light.	Dark.	Light.	Dark.	Light.	Dark.
1	0.40 g.	0.1645 g.	0.2729 g.	0.0108 g.	0.0040 g.	56.0%	37.7%
2	0.20	0.0658	0.0949	0.0041	0.0005	65.0	52.0
3	0.10	0.0140	0.0406	0.0024	0.0002	83.0	58.8
4	0.05	0.0130	0.0212	0.0016	0.0000	81.0	58.0

TABLE I (contd.)

## III. Ammonium phosphate solutions exposed from 21-1-47 to 7-3-47. (Mean temp. = 35.5°).

No.	Original N per 100 c.c. soln.	NH <sub>3</sub> -N left un-oxidised in		Nitric-N formed in		Loss of N in	
		Light.	Dark.	Light	Dark.	Light.	Dark
1	0.40 g.	0.1780 g.	0.2030 g	0.0072 g.	0.0034 g.	53.7%	48.4%
2	0.20	0.0200	0.0284	0.0030	0.0010	88.5	85.0
3	0.10	0.0005	0.0008	0.0008	0.0001	98.7	99.1
4	0.05	0.0000	0.0002	0.0000	0.0000	100.0	99.8

## IV. Ammonium perchlorate solutions exposed from 21-7-47 to 27-9-47. (Mean temp. = 35.5°).

1	0.40 g.	0.2299 g.	0.2811 g.	0.0027 g.	0.0016 g.	41.8%	29.3%
2	0.20	0.0925	0.1132	0.0014	0.0010	53.0	42.9
3	0.10	0.0324	0.0413	0.0009	0.0005	66.7	58.2
4	0.05	0.0116	0.0160	0.0005	0.0001	75.8	67.9

## V. Ammonium dichromate solutions exposed from 21-7-47 to 27-9-47 (Mean temp. = 35.5°).

1	0.40 g	0.3227 g	0.3600 g.	0.0028 g.	0.0020 g.	18.6%	9.5%
2	0.20	0.1146	0.1531	0.0016	0.0012	41.9	22.8
3	0.10	0.0497	0.0579	0.0008	0.0006	49.5	42.0
4	0.05	0.0152	0.0258	0.0006	0.0004	68.4	47.6

## VI. Ammonium nitrate solutions exposed from 21-7-47 to 27-9-47. (Mean temp. = 35.5°).

1	0.80 g.	0.2388 g	0.2785 g.	0.3727 g.	0.3765 g.	23.5%	18.5%
2	0.40	0.0801	0.1101	0.1872	0.1904	33.2	24.8
3	0.20	0.0265	0.0366	0.0896	0.0906	41.9	36.4
4	0.10	0.0105	0.0150	0.0450	0.0464	44.5	38.6

The above experimental results with all ammonium salts excepting ammonium nitrate show that a considerable amount of the ammonium salt is oxidised and an appreciable amount of nitric nitrogen is formed in every case. The effect of sunlight is found to be very marked in all the cases, the amount of ammonium salts oxidised being always greater in the salts exposed to sunlight than those kept in the dark. Also, the amount of nitric nitrogen formed in the exposed flasks is much greater than that formed in the covered ones.

If the nitrification of ammonium salts were only of bacterial origin, as it is generally believed, and not a photochemical and surface oxidation reaction, the ammonium salts in the covered sets should have also undergone oxidation at least to the same extent as the exposed ones. On the other hand, our results definitely go to show that, whilst large amounts of ammonium salts are oxidised to nitrite and nitrate in presence of light, much less oxidation and nitrate formation of ammonium salts take place in the covered vessels.\* It appears therefore that nitrification of ammonium salts is to a large extent an induced surface oxidation reaction aided by light radiations.

Another important point brought out by these results is that the process of nitrification is always associated with nitrogen loss. In the case of loss also, the factor of light radiations plays an important part; the loss in the exposed sets is found to be always greater than the loss in the covered sets.

The loss of nitrogen has been explained by us from the view point that during nitrification, ammonium nitrite is produced as an intermediate product and this readily decomposes into water and nitrogen gas which escapes and causes the loss.

As the oxidation of ammonium salts is always more pronounced in light than in the dark, there is always the possibility of greater amounts of ammonium nitrite formation in the sets exposed to light than in the dark and hence there is always more nitrogen loss found in the exposed sets than in the covered ones.

It is to be seen from the results that the greater the initial nitrogen content, the greater is the loss of nitrogen, though the percentage loss increases with dilution. Though at first consideration the greater percentage loss with dilution seems unexpected, but a closer analysis of these results reveals the marked influence of surface on the reaction. The amount of calcium carbonate (used as surface) in all the concentrations of the solution is the same and the volume of the solution is also the same; hence the possibility of an ammonium ion coming in contact with the active centres of the surface is increased on increasing the dilution of the ammonium salt. When the concentration of the ammonium ions is increased, the total number of ions coming in contact with the active centres is also increased, but the percentage of the ions coming in contact with surface is decreased. On the other hand, with increase in dilution, the total number of ions coming in contact with the surface, though decreased, yet the percentage of ions coming in contact with the active spots of the surface is increased, and as a result of this the percentage loss of nitrogen is found to be more in the lower concentrations of the ammonium salt solutions.

Moreover, there is a slight loss of ammonia gas in these experiments, as calcium carbonate is slightly alkaline.

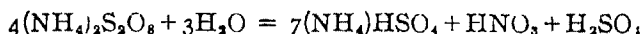
The experimental results show clearly that the loss is maximum with ammonium phosphate. This is due to the fact that there is a double decomposition between calcium carbonate and ammonium phosphate with the formation of calcium phosphate and ammonium carbonate, which slowly decomposes into carbon dioxide and ammonia.

The loss with other substances is in the following decreasing order: ammonium phosphate, ammonium sulphate, ammonium perchlorate, ammonium dichromate, ammonium nitrate and ammonium persulphate.

It appears that with ammonium persulphate the loss of nitrogen is the least. With ammonium dichromate and nitrate, though the loss is greater than with ammonium persulphate, yet, is less than with other ammonium salts. These results showing different losses with different ammonium salts, specially when the acid ion is an oxidising one, is of considerable interest. Moreover, the results with ammonium nitrate show that the nitric nitrogen in the system is appreciably less after the exposure than the original amount of nitric ion introduced. This is due to the fact that the free ammonium hydroxide obtained by the action of calcium carbonate and ammonium nitrate is partially lost by escape of free ammonia gas and another part of the ammonium

hydroxide reacts with the nitrate ion forming nitrite ion which in combination with ammonium ion decomposes as nitrogen gas. This reduction of nitrate ion to nitrite appears to be more prominent in light than in the dark and hence the nitric nitrogen present in the system after exposure is always appreciably less than in the system kept in the dark.

It is generally believed that ammonium persulphate decomposes in the following manner in aqueous solutions:



It appears that in this process small amounts of nitrous acid is also formed and this decomposes according to the equation,



With ammonium persulphate the loss of nitrogen is the least because in presence of acids, ammonium nitrite cannot exist but it forms nitrous acid. Moreover, the nitric nitrogen with ammonium persulphate is much higher than with other ammonium salts (24.1 mg. in the highest concentration in light while 10.8 mg. under similar conditions in ammonium sulphate and 7.2 mg. in ammonium phosphate). This is due to the fact that the ammonium ion in this case is oxidised chiefly by the persulphate ion into nitric acid, whilst with the other ammonium salts the oxidation is mainly caused by the dissolved oxygen and the process is much slower.

#### C O N C L U S I O N

The results show that ammonium salts are nitrified on exposure to light.

The amount of salt oxidised is greater in light than in the dark, also the amount of nitrate formed is much more in exposed sets than in the covered ones.

During nitrification a considerable amount of nitrogen is lost as gaseous nitrogen due to decomposition of the intermediate compound, ammonium nitrite, formed during the reaction.

Light seems to have an important effect on the amount of nitrogen loss, the loss being always greater in sunlight than in the dark.

Greater the initial nitrogen, the greater is the loss, though the percentage loss increases with decreasing concentration of ammonium salts.

Nitrification seems to be partly surface oxidation reaction catalysed by sunlight.

Loss of nitrogen is maximum with ammonium phosphate and minimum with ammonium persulphate.

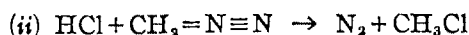
With ammonium nitrate, the nitrate content after exposure is less in the exposed vessels than the original concentration of nitrate ion. This is due to the reaction between ammonia and nitrate ion and the formation of ammonium nitrite.

## SPONTANEOUS DECOMPOSITION OF $\omega$ -DIAZO-*O*-METHOXY- ACETOPHENONE

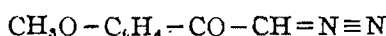
BY UPKARI SINGH SETH AND S. S. DESHPANDE

$\omega$ -Diazo-*O*-methoxyacetophenone has been synthesised in crude form. The liquid diazo-ketone decomposes spontaneously with loss of nitrogen and deposition of a solid ketone of the composition  $C_9H_8O_2$ , characterised by its semicarbazone. The diazo-ketone gives by Arndt-Eistert synthesis *O*-methoxyphenylacetamide. The solid ketone adds bromine and forms a dibromide,  $C_9H_8O_2Br_2$ . It is inferred that in the formation of solid ketone the radical of diazo-ketone undergoes some rearrangement other than the Wolff rearrangement.

A method for preparing diazo-ketones  $R-CO-CH=N\equiv N$  in satisfactory yields from the corresponding acid chloride,  $R.CO.Cl$  has been described by Robinson and Bradley (*J. Chem. Soc.*, 1928, 1310). It consists in adding an ethereal solution of the chloride (1 mol.) to ethereal solution of an excess (2.5 mol.) of diazomethane at  $-10^\circ$ . Nitrogen is slowly evolved due to the action of hydrochloric acid formed in (i) on the excess of diazomethane.

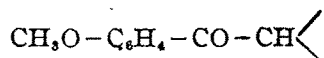


We used this process and treated *O*-methoxybenzoyl chloride (1 mol.) with diazomethane (2.5 mol.) in ether. After completion of the reaction and evaporation of the solvent at room temperature under reduced pressure  $\omega$ -diazo-*O*-methoxyacetophenone (I) was left in crude form as a liquid in an almost quantitative yield.



(I)

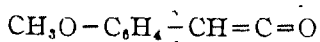
The crude diazo-ketone, right from the time of its isolation from the solvent, began to decompose spontaneously and continuously at room temperature, losing a gas in minute bubbles. When the tube containing the liquid ketone was corked, an appreciable pressure was developed in a few minutes due to accumulation of nitrogen. Simultaneously a pale yellow crystalline solid was slowly being deposited. The latter on examination was found to be free from nitrogen. It melted at  $104^\circ$  and gave on analysis results agreeing with the composition  $C_9H_8O_2$ , which is that of the radical



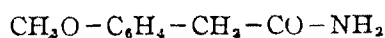
(II)

The existence of the diazo-ketone (I) in the liquid was proved as follows: By the action of ammonia on the freshly prepared liquid in presence of silver nitrate (catalyst) in dioxane, the Arndt-Eistert synthesis expected of diazo ketones took place (*Ber.*,

1935, 68, 200). An amide (m.p. 131°) was obtained having the composition  $C_9H_{11}O_2N$ . Hydrolysis of the amide gave an acid, identified as *O*-methoxyphenylacetic acid. The amide is therefore *O*-methoxyphenylacetamide (IV) formed, as expected, by the Wolff rearrangement of the radical (II) to the ketene (III) which subsequently adds ammonia to give the amide.



(III)

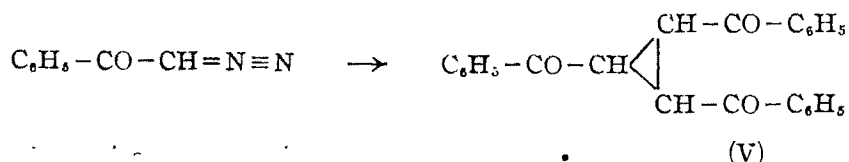


(IV)

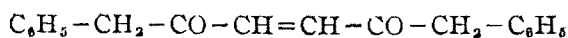
The solid (m.p. 104°) gives a semicarbazone (m.p. 220°) whose analysis gives results corresponding with the composition  $C_{10}H_{11}O_2N_3$  which is that of the semicarbazone of the ketone  $C_9H_8O_2$ . It is noteworthy that addition of semicarbazide hydrochloride and sodium acetate to the crude liquid diazo-ketone gives the same semicarbazone as that of the nitrogen-free solid. Since during the period of semicarbazone formation (one day) nitrogen is evolved, it is inferred that the diazo-ketone turns into nitrogen-free solid and the semicarbazone formed is that of the latter compound.

The observation about the semicarbazone does not give information about the mass and structure of the molecule of the solid beyond the fact that one  $C_9H_8O_2$  unit reacts with one molecule of semicarbazide.

Thermal decomposition of diazo-ketones in amyl ether at temperatures exceeding 110° was studied by Schroeter (*Ber.*, 1916, 49, 2743) who observed quantitative evolution of nitrogen and formation of oily residues in which neither the dimers of ketenes nor the isomeric cyclobutane diones could be identified. Grundmann (*Annalen*, 1938, 536, 29) observed thermal non-catalysed decomposition of  $\omega$ -diazoacetophenone and showed that the decomposition product was *cis*-1:2:3-tribenzoylcyclopropane (V)



(V)



(VI)

The decomposition under similar conditions of the diazo-ketone, prepared from phenylacetyl chloride, catalysed by cupric oxide, affords, however,  $\alpha\beta$ -diphenylacetylene. The decomposition of  $\omega$ -diazo-*O*-methoxyacetophenone (I) is non-catalysed and spontaneous, and therefore differs somewhat from cases of decomposition cited above. Whether the radical formed from a molecule of a diazo-ketone after loss of nitrogen, polymerised to a cyclopropane or ethylenic compound, could be ascertained from the knowledge about the molecular weight of the product of polymerisation. In the case of the solid (m.p. 104°) the value of the molecular weight found by cryoscopic method in benzene came to be 140 ( $C_9H_8O_2$ , M.W. = 148).

The solid (m.p.  $104^\circ$ ) is neutral in reactions and can be crystallised from boiling water unchanged. In contact with aqueous ferric chloride it develops a dark violet colour after prolonged standing. Its solution in carbon tetrachloride absorbs bromine very slowly at  $0^\circ$  in diffused daylight. A small proportion of hydrobromic acid gas is also evolved. The solid bromo compound left after removal of the solvent and after crystallisation melted at  $147^\circ$ . The result of its analysis corresponds with the composition  $C_9H_8O_2Br_2$ . Neither the cyclopropane nor the ethylenic structure is therefore admissible for the solid.

The observations so far made indicate that the radical (II) undergoes some rearrangement other than the Wolff rearrangement to produce a stable molecule capable of accepting two atoms of bromine slowly. The nature of this rearrangement will become clear in the light of further work we are doing on the compound.

#### EXPERIMENTAL

*$\omega$ -Diazo-o-methoxyacetophenone.*—O-Methoxybenzoyl chloride (b.p.  $180^\circ/120$  mm., 6.5 g., 1 mol.), dissolved in dry ether, was slowly added to an ethereal solution of diazomethane, prepared from 18.8 g. of nitrosomethylurea (the solution contained about 4 g., 2.5 mol. of gaseous diazomethane). The temperature was maintained at  $-10^\circ$  and the addition spread over a period of 1 hour. Nitrogen was slowly evolved. The reaction mixture was kept at  $0^\circ$  for 4 hours and then at room temperature overnight. The solvent was then removed by evaporation under reduced pressure at room temperature. The crude diazo-ketone weighed 6.8 g.

*Formation of the Decomposition Product.*—The crude diazo-ketone began to decompose spontaneously with loss of nitrogen and deposition of a solid. From 3 g. of the diazo-ketone 1.5 g. of the solid were collected during 2 days. The rate of decomposition fell with lapse of time. The pale yellow crystalline deposit is soluble in usual organic solvents and separates from hot dilute alcohol in pale yellow short prisms, m.p.  $104^\circ$ . [Found: C, 72.5; H, 4.7; M. W. (cryoscopic in benzene), 140.  $C_9H_8O_2$  requires C, 72.9; H, 5.4 per cent. M. W., 148].

The semicarbazone of the solid compound (m.p.  $104^\circ$ ) crystallises from hot dilute alcohol in small needles, m.p.  $220^\circ$ . (Found: N, 21.2.  $C_{10}H_{11}O_2N_3$  requires N, 20.5 per cent).

Addition of semicarbazide hydrochloride and sodium acetate to the crude liquid diazo-ketone yielded a semicarbazone after standing for 1 day. Crystallised from alcohol it melted at  $220^\circ$  and when mixed with the semicarbazone of the solid produced no depression in its melting point.

*The Bromine Addition Product of the Solid.*—The solid (m.p.  $104^\circ$ , 0.3 g.) was dissolved in carbon tetrachloride (4 c.c.) and to the solution cooled by ice, bromine dissolved in the same solvent was added until red colour persisted. Hydrobromic acid was evolved in small proportion. The bromide left after evaporation of the solvent at room temperature is a yellow solid which crystallises from alcohol in clustering needles, m. p.  $147^\circ$ , yield 0.3 g. (Found: Br, 53.1.  $C_9H_8O_2Br_2$  requires Br, 52.0 per cent).

*O-Methoxyphenylacetamide.*—The freshly prepared diazo-ketone (3 g.) was dissolved in dioxane (20 c.c.) and 30% solution of ammonia (20 c.c.) and 10% solution of silver

nitrate (3 c.c.) were added. The mixture was left overnight and then refluxed on a water-bath for 4 hours. The precipitated silver oxide was filtered and the filtrate evaporated on the water-bath when a white solid mixed with black silver residue was left. The former was extracted with ether and after removal of the solvent the crude amide weighed 1.5 g. and it was purified by crystallisation from dilute alcohol. The pure amide melts at  $131^{\circ}$ . (Found: N, 9.3.  $C_9H_{11}O_2N$  requires N, 8.5 per cent).

The amide was heated with aqueous caustic potash until no more ammonia evolved. On cooling and acidifying the clear solution an oily emulsion was obtained from which on standing a crystalline solid acid separated. It crystallises from hot water in small needles, m. p.  $124^{\circ}$ . *O*-Methoxyphenylacetic acid melts at  $124^{\circ}$ . (Found: Equiv., 165.0.  $C_9H_{10}O_3$  requires equiv., 166.0).

The authors thank Shri Ishwari Prashad Agarwal of these laboratories for his help in the work.

CHEMICAL LABORATORIES,  
AGRA COLLEGE, AGRA.

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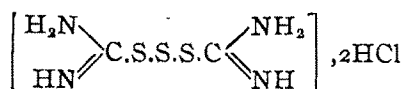


# INTERACTION OF SULPHUR MONOCHLORIDE WITH THIOCARBAMIDE AND THIOCARBANILIDE

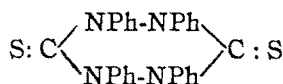
By R. H. SAHASRABUDHEY

Sulphur monochloride reacts in an inert solvent medium with thiocarbamide and thiocarbanilide forming salts of "formamidine disulphide" and phenylaminobenzthiazole respectively; a trisulphide or a tetrazine is not produced as postulated by Naik. The mechanism of its reaction with thiocarbamides and allied compounds has been discussed.

The interaction of sulphur monochloride with thiocarbamide and thiocarbanilide has been investigated by Naik (*J. Chem. Soc.*, 1921, 119, 1166); formation of "sulphidodithiocarbamide dihydrochloride", a trisulphide (I) and of "3:6-dithio-1:2:4:5-tetraphenylhexahydro-1:2:4:5-tetrazine" (II) respectively, has been reported,

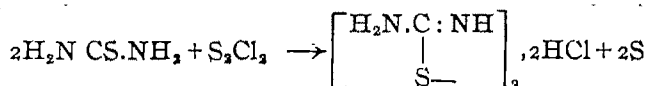


(I)



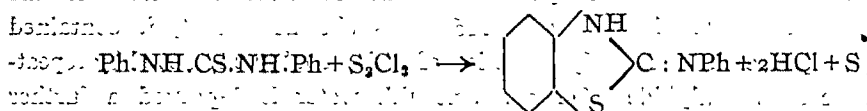
(II)

From the reactions of thiocarbamide with certain acid chlorides (*J. Chem. Soc.*, 1886, 49, 190; 1887, 51, 378, 666; 1912, 101, 2171) it appears that under the conditions of the experiment thiocarbamide should form "formamidine disulphide" rather than the above trisulphide. Thus:



Formamidine disulphide dihydrochloride.

The tetrazine constitution (II) for the product from thiocarbanilide has been proposed (Naik, *loc. cit.*) by analogy with the compounds of Hector (*J. prakt. Chem.*, 1892, ii 44, 492; 48, 200; *Ber.*, 1889, 22, 1176; 1890, 23, 357) and Dost (*Ber.*, 1906, 39, 1014). The constitution of Hector's compounds cannot, however, be regarded as finally settled (this *Journal*, 1939, 16, 32) and contrary to the postulates of Dost it has been shown (Sahasrabudhey and Krall, this *Journal*, 1944, 21, 17) that sulphur monochloride reacts with NN-methylphenylthiocarbamide in chloroform medium forming 1-amino-2-methyl-1:2-dihydrobenzthiazole and not a cyclic disulphide or a hydrazodithiocarbonamide. In the case of thiocarbanilide also, the reaction is therefore expected to take an analogous course:



As will be evident from the experimental part, both these expectations have been realised.

Attempts at the oxidation of thiocarbamides with sulphur monochloride in aqueous, acid or dilute alcoholic media were not successful.

**Mechanism of the Reaction.**—The interactions of  $S_2Cl_2$  with amides, thioamides, thiocarbamides and thiols appear to belong mainly to two groups: (i) where the sulphur atom is directly involved and (ii) where it is the amino group that reacts. In the investigations of Chakravarty (*J. Chem. Soc.*, 1923, 123, 964; *J. Ind. Inst. Sci.*, 1930, 13A, 73, 85) and S. Ishikawa (*Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1925, 2, 299; 1925, 3, 147; 1927-1928, 7, 237) the first mechanism appears to be operative, while studies by Naik (*J. Chem. Soc.*, 1921, 119, 1166) reveal the occurrence of the second mechanism.

A review of the work of these authors and other pertinent literature shows that the above two groups of reactions can be subdivided into two further categories: (A) where  $S_2Cl_2$  gets condensed, and (B) where it acts as a mere oxidising agent with the elimination of sulphur and HCl. The reactions of thioamides and thiocarbamides belong to group (i) and (B) category (*Sci. Rep. Tokyo Bunrika, Daigaku, Sec. A*, 1934-1935, 2, 17; *Ber.*, 1914, 47, 699, 703; Ray and Das, *J. Chem. Soc.*, 1922, 121, 323).

In view of the above considerations, the controversy about the exhibition of tautomerism by thiocarbamides and the work of Hunter (*this Journal*, 1931, 8, 147; 1932, 9, 435, 357, 545, *et seq.*), Dixon (*J. Chem. Soc.*, 1907, 91, 122, 912; 1908, 93, 18; 1920, 117, 80, 720; 1924, 243), Zincke (*Ber.*, 1910, 43, 837; 1909, 42, 2721, 3362, 2275, 2282), Fromm (*Annalen*, 1910, 374, 90; 1915, 394, 284), Hagershoff (*Ber.*, 1901, 34, 3130, 3136; 1903, 36, 3121) and others, it appears that the primary reaction of a thiocarbamide with  $S_2Cl_2$  should result in an initial anchoring of the acid chloride molecule on the sulphur atom of these compounds. Such a union is necessarily unstable, and the halogen eventually migrates on to one of the amino nitrogens forming a N-halide which in the case of aromatic thiocarbamides most probably undergoes a rearrangement analogous to the intramolecular type of chloramine transformation or/and causes excitation followed by elimination of the nuclear *o*-hydrogen and finally ring-closure giving a benzthiazole.

McClelland and Warren (*J. Chem. Soc.*, 1930, 1095) believe that the oxidation of thioamides and thioanilides to thiazoles takes place through the intermediate formation of disulphides; this view, however, does not find support from a study of the oxidation of aromatic thiocarbamides (Sahasrabudhey and Krall, *this Journal*, 1945, 22, 37).

#### EXPERIMENTAL

**Action of Sulphur Monochloride on Thiocarbamide in absolute Alcohol and Chloroform.**—The reaction was carried out as described by Naik and also with varying quantities of reactants. In all cases, a hard yellow mass, identical in its behaviour with the previously described product (Naik, *loc. cit.*, p 1169) was obtained. But, it contained sulphur in varying proportions and only a fraction of which could be removed by repeated extraction with carbon disulphide. On treatment with water it deposited a further

quantity of sulphur. The aqueous extract was strongly acidic and corresponded fully to the description given by Naik.

It is not possible to crystallise the yellow mass from any of the more common solvents and since it contains varying proportions of sulphur, it cannot be considered as a definite compound. Sulphur is most probably held in a sort of pseudo solution by "formamidine disulphide" which is the principal product of the reaction (*vide infra*).

The identity of the product in the aqueous extract with formamidine disulphide has been proved by the following facts: (i) It liberated iodine from aqueous potassium iodide solutions. (ii) On treatment with dilute nitric and picric acids a nitrate (m.p.  $138^{\circ}$  d.) and picrate (m.p.  $154^{\circ}$  d.) were obtained. Identity of these with the nitrate and picrate of formamidine disulphide (Werner, *loc. cit.*) was established by undepressed mixed melting points taken with genuine samples. (iii) The aqueous extract on boiling or treatment with alkali deposited sulphur, and on evaporation crystals of thiourea were obtained along with a syrupy viscous residue which proved to be cyanamide.

The reaction of  $S_2Cl_2$  on thiocarbamide was also carried out in chloroform medium with identical results.

*Action of Sulphur Monochloride on Thiocarbamilide in Benzene and Chloroform.*—

The reaction was carried out according to Naik's procedure. Prismatic crystals melting at  $159^{\circ}$  (Naik gives m.p.  $160^{\circ}$ ) were obtained in a small quantity. On treatment with acetic anhydride they gave an acetyl derivative, m.p.  $162-63^{\circ}$ .

The identity of these compounds with phenylaminobenzthiazole, prepared by the action of bromine on thiocarbamilide according to Hegershoff's procedure and its acetyl derivative respectively, was established by undepressed mixed melting points.

As the yield of the product was very poor, in view of the brisk reaction between  $S_2Cl_2$  and thiocarbamilide solution, it appeared that heating for a long time (3 hours in the above experiment) might have led to secondary changes. Following procedure was found satisfactory:

Thiocarbamilide (4 g.) was taken in about 50 c.c. of the solvent (benzene or chloroform) and 2 c.c. of  $S_2Cl_2$  in 10 c.c. of the same solvent were gradually added. The mixture was warmed on a water-bath under a reflux condenser for about 20-30 minutes when the initially brisk evolution of HCl slackened. On evaporation of the solvent, a yellow, sticky residue was left behind, which on extraction with 50 c.c. of rectified spirit gave 3.6 g. of a crude crystalline product. It was crystallised twice from alcohol, m.p.  $159^{\circ}$ ; and gave an acetyl derivative, m. p.  $162-63^{\circ}$ .

The author wishes to express his thanks to Prof. H. Krall for his interest and to Principal S. S. Joshi and Prof. P. S. Varma for the facilities.

CHEMISTRY DEPARTMENT,  
COLLEGE OF SCIENCE,  
BANARAS HINDU UNIVERSITY.

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## ESSENTIAL OIL FROM THE RESIN OF *COMMIPHORA* *MUKUL*, HOOK. EX. STOCKS

By ASHARAM BHATI

The chief components of the essential oil from the resin of *Balsamodendron Mukul* are 64% myrcene, 11% dimyrcene, and some polymyrcene.

*Commiphora Mukul*, a small tree of the Burseraceae family, is found on the rocky ground in the arid zones of Rajputana and Khandesh. An oleo-resin exudes naturally or from incisions made on the bark in the cold season. This brownish or greenish resin, with an attractive perfume, is popularly known as "Gugal" (Mahisakshi Gugal) and is used as an incense and also as a drug in the treatment of rheumatism.

R. N. Chopra ("Indigenous Drugs of India", 1933, p. 287) mentions that *Commiphora mukul* is allied to *Commiphora myrrha* which is indigenous to North-East Africa, and which contains from 2.5 to 10% of an essential oil. He mentions that although the resin from the first is not worked up like that from the second, the essential oil components of the first will be very similar to those from the second. These are cumaldehyde, eugenol, cresol, pinene and dipentene.

An essential oil from the resin of *Commiphora mukul* has been described by D. Satyanarayan Naidu (*Proc. Indian Sci. Cong.*, 1927, p. 104) who extracted the resin with light petrol and obtained a viscous, golden yellow liquid which on distillation under reduced pressure gave two fractions. These fractions do not appear to have been worked up, but are merely described as esters. Essential oil from the gum resin was also extracted by Dutt, Ghosh and Chopra (*Ind. J. Med. Res.*, 1942, 30, 33) who report an yield of 1.45% of the essential oil.

With a view to studying the chemistry of the volatile components of this medicinally important resin, and further to ascertaining whether the medicinal properties are on account of the volatile or the non-volatile part of the resin, the author undertook the present work. As will be seen from what follows our observations do not agree with those recorded or suggested by the authors referred to above.

The fresh resin was collected under the personal supervision of the author from the arid zones around Jaisalmer in Rajputana in September last year, and it was definitely ascertained that the product we were dealing with was from the plant *Commiphora mukul*.

On steam-distillation, the resin affords a yellowish white oil in 0.37% yield with fragrant smell resembling that from unripe mangoes. It has the following physical and chemical constants. Those of the oil from *Commiphora myrrah* are also shown alongside for comparison.

TABLE I

*C. Mukul.* $d_{20}^{25}$ , 0.8278 $n_D^{25}$ , 1.4800 $[\alpha]_D^{25}$ , 0°

Sapon. value, 50

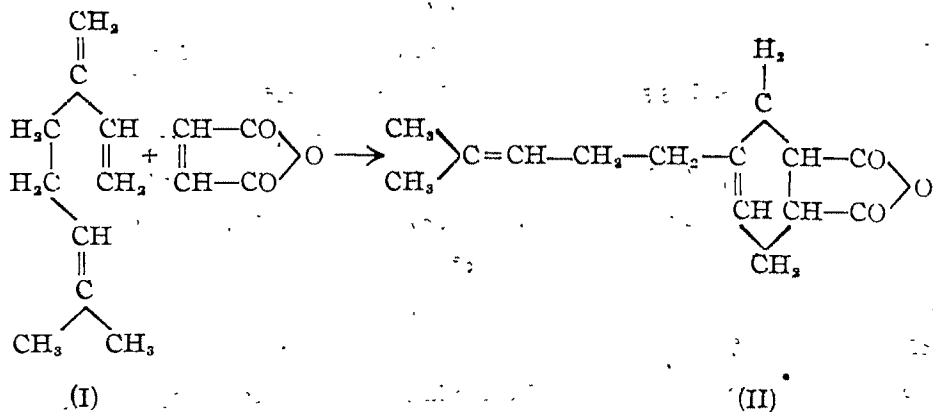
*C. Myrrah.* $d_{15}^{20}$ , 0.988—1.024\* $n_D^{20}$ , 1.5196—1.5274\* $[\alpha]_D^{20}$ , 29—93\*

Sapon. value, 16—40\*

\*Gildemeister and Hoffmann, 3rd Ed., Vol. III, p. 152.

Fractionation of the oil gave two fractions with fairly constant boiling points. Fraction (I), constituting about 64% of the oil, seemed to be a single compound, as on repeated distillation it boiled within the narrow range of 168°–170°. Its preliminary quantitative analysis showed that it was a hydrocarbon mixed with a small amount of some oxygen-containing compound. This was removed by distillation over sodium. The pure compound, so obtained, gave on analysis results agreeing with the formula  $C_{10}H_{16}$  of a terpene. This absorbed bromine but did not give a solid bromine addition compound. Nor did it give a solid derivative such as a nitrosite or a nitrosochloride. An additional difficulty about the terpene was that it could not be kept long without polymerisation. The polymerised product distilled at the temperature of fraction (II) described later, and from comparison of the properties it appeared that fraction (I) polymerised to fraction (II).

The high degree of unsaturation of the compound suggested that it was probably an open-chain terpene. This inference has been proved to be correct from its molecular refraction [found: M. R., 46.85; M. R. for  $(C_{10}H_{16})_3$ , 46.66] and by the fact that it combined with maleic anhydride by the process of Diels and Alder (*Annalen*, 1929, 470, 81) and gave an adduct melting at 33–34°. On hydrolysis, the adduct gave a dicarboxylic acid with a wide melting range of 106° to 114°. By repeated crystallisation from ethyl acetate, the melting range could be narrowed to 110°–114°, but the homogeneity of the crystalline form and the purity of the acid still remain uncertain.



The acid, however, forms a characteristic, sparingly soluble, crystalline acid potassium salt. By decomposing this salt with an acid the dicarboxylic acid melting at 112-114° was obtained. From the m.p. of the adduct of maleic anhydride with the terpene, and that of the dicarboxylic acid by hydrolysis of the latter, as also from the analysis of the corresponding acid potassium salt, the terpene seems to be myrcene (I) and the adduct is 4-isohexenyltetrahydrophthalic anhydride (II).

A comparison between the properties of myrcene and its derivatives with those of our compound and its derivatives is made in Table II.

TABLE II

Properties.	The compound.	Myrcene.	References.
B.p.	106°-109°/120 mm. or 168°-170°/750 mm.	51°-53°/10 mm.	(Farmer & Sutton, <i>J Chem Soc</i> , 1942, 145). (Semler, <i>Ber</i> , 1901, 34, 3126)
Density	0.8070 at 30°	0.8028 at 15°	(Eijkman, <i>Chem. Zentr.</i> , 1907, II, 1211)
$n_D$	1.4680 at 31°	1.4722 at 30°	(Eijkman, <i>loc cit.</i> )
M.R.	45.85	$C_{10}H_{16}/3$ , 46.66	
M.p. of the maleic anhydride adduct	33-34°	34-35° 122-123°	(Diels & Alder, <i>loc. cit.</i> ) (Diels & Alder, <i>loc. cit.</i> )
M p. of the dicarboxylic acid	112-114°	111.5-113.5°	(Arbusow & Abramow, <i>Ber.</i> , 1934, 67, 1942).

Fraction (II) from the result of analysis and molecular weight determination seemed to be a hydrocarbon of the composition  $C_{20}H_{32}$ . Its formation from myrcene on keeping and to some extent on distillation suggests that it is possibly dimyrcene. This has been proved to be correct. In chloroform solution it absorbs bromine and with nitrogen trioxide forms a nitrosite which melts with decomposition at 160°. Its various properties are recorded in Table III.

TABLE III

Properties.	The compound.	Dimyrcene.	References.
B. p.	176°-178°/5.5 mm.	183°-184°/10 mm.	(Lebedev, <i>J Russ. Phys. Chem. Soc.</i> , 1913, 45, 1249, 1396).
Density	0.9041 at 30°	0.8763 at 20°	(Lebedev, <i>loc. cit.</i> )
$n_D$	1.5010 at 30°	1.49859 at 20°	(Lebedev, <i>loc. cit.</i> )
$[\alpha]_D$	0°	0°	
M.R.	88.63	$C_{20}H_{32}/3$ , 88.61	
M.p. of nitrosite	160° with decomposition	163° with decomposition	(Harries, <i>Ber.</i> , 1902, 35, 3254)

The behaviour of the diterpene from the resin is exactly like that of dimyrcene from para rubber described by Harries (*loc. cit.*). He mentions that after distilling the diterpene a residue is left which he calls polymyrcene and which with nitrogen trioxide in benzene solution gives a nitrosite melting with decomposition at  $163^{\circ}$ . We also obtained a similar residue after distilling off the diterpene and this gave with nitrogen trioxide in benzene solution a nitrosite which melted with decomposition at  $163^{\circ}$ . It will thus be seen that the characteristics and constituents of the essential oils from *C. mukul* and *C. myrrah* bear little resemblance to each other.

#### EXPERIMENTAL

*Isolation of the Essential Oil.*—The essential oil was obtained by steam-distillation of the resin (5 kilos) from a copper still fitted with a spiral copper condenser. The oil (12.5 c.c.) floating over the aqueous distillate was collected and from the aqueous layer 9.5 c.c. more were obtained by extraction with  $\text{CCl}_4$ . The total yield of the oil ( $12.5 + 9.5 = 22$  c.c.) was thus 0.37% of the weight of the resin.

*Fractionation of the Oil.*—The oil (36 c.c.) was fractionally distilled and the following fractions were obtained :

No.	B.p.	Vol.	Yield.
I.	$106^{\circ}\text{--}109^{\circ}/12^{\circ}$ mm. or $168^{\circ}\text{--}170^{\circ}/750$ mm.	23.1 c.c.	64%
	Between $90^{\circ}\text{--}176^{\circ}/5.5$ mm. (I and II)	7.5	20
II.	$175^{\circ}\text{--}177^{\circ}/5.5$ mm.	4	11
Residue	Above $178^{\circ}/5.5$ mm.	1.4	5

*Isolation of Pure Myrcene from Fraction (I).*—Preliminary analysis showed that this fraction was a hydrocarbon mixed with a small percentage of an oxygen containing compound. Hence it was distilled over sodium under reduced pressure and once more distilled at ordinary pressure. It was then analysed. [Found: C, 87.9; H, 11.6; M.W. (cryoscopic in benzene), 142; M.R., 46.85.  $\text{C}_{10}\text{H}_{16}$  requires C, 88.2; H, 11.8 per cent. M. W. 136; M.R./3, 46.66].

*The Maleic Anhydride Adduct.*—The pure terpene (2.6 c.c.) from fraction (I) was dissolved in dry benzene (6 c.c.) and the solution gradually added to a suspension of maleic anhydride (1.9 g.) in 5 c.c. of benzene. The reaction started within five minutes and the temperature rose from  $16^{\circ}$  to  $33^{\circ}$ . The mixture was allowed to remain at the room temperature for half an hour and then heated in a well-corked bottle (to exclude moisture) in a water-bath for 4 hours. The residue left on removal of the solvent was cooled in ice when a white solid separated, m.p.  $33\text{--}34^{\circ}$ , yield 3 g.

*The Acid Potassium Salt.*—The crude maleic anhydride adduct was hydrolysed with theoretical proportion of 30% KOH solution. Within 5 minutes of warming the mixture on a water-bath a sparingly soluble potassium salt of the corresponding dibasic acid separated. This was filtered and washed with ether to free it from unreacted terpene. It was then decomposed with 10% sulphuric acid when a thick

yellow oil separated which solidified on standing. The solid acid was filtered, washed with water and dried. It melted at  $106^{\circ}$ - $114^{\circ}$ , but could not be obtained in definite crystalline form from usual organic solvents; although by repeated crystallisations from ethyl acetate the melting range could be narrowed to  $110^{\circ}$ - $114^{\circ}$ . Arbusow and Abramow (*loc. cit.*) used methyl cyanide to crystallise this acid, but even then they could not get it in a sharply melting range. The acid was therefore converted into its acid potassium salt by warming it with molecular proportion of 30% caustic potash. On keeping the solution, so obtained, overnight, the acid potassium salt separated in fine white crystals, m.p.  $150$ - $51^{\circ}$ . (Found:  $\text{K}$  equiv., 288.1.  $\text{C}_{14}\text{H}_{18}\text{O}_4\text{K}$  requires equiv., 290).

*Dimyrcene from Fraction (II).*—Fraction (II) even on further distillation boiled at  $176^{\circ}$ - $178^{\circ}/5.5$  mm. It was then analysed. [Found: C, 88.0; H, 11.5; M.W. (cryoscopic in benzene), 259; M.R., 88.63.  $\text{C}_{20}\text{H}_{32}$  requires C, 88.2; H, 11.8 per cent. M.W., 272; M.R.  $\frac{1}{3}$ , 88.61].

*The Dimyrcene Nitrosite.*—Fraction (II) (2 c.c.) was dissolved in 10 c.c. of dry benzene and through this well cooled solution a stream of nitrogen trioxide (generated from arsenious oxide and strong nitric acid) was passed till saturation. A gummy product separated which on drying hardened and could be powdered. It was then dissolved in minimum quantity of ethyl acetate and reprecipitated with absolute ether. The pure nitrosite melts at  $160^{\circ}$  with decomposition. [Found: N, 14.0.  $(\text{C}_{10}\text{H}_{16}\text{N}_3\text{O}_7)_2$  (Harries, *loc. cit.*) requires N, 14.5 per cent].

The nitrosite of the polymyrcene was obtained similarly from the residue from the distillation of the oil. It melts with decomposition at  $160^{\circ}$ .

#### CONCLUSION

The medicinal properties of myrcene or of its polymerides are not found on record and as these form the chief components of the essential oil from the resin it is not possible to say at this stage whether the medicinal properties of Gugal are on account of its volatile components. Probably these properties reside in the non-volatile part.

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CHEMICAL LABORATORIES,  
AGRA COLLEGE, AGRA.

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## ESSENTIAL OIL FROM THE GALLS OF *PISTACIA INTEGERREMA*

BY K. K. BASLAS AND S. S. DESHAPANDE

The essential oil from the galls of *Pistacia integerrema* consists of 94% of  $\alpha$ -d-pinene as the chief component.

The plant *Pistacia integerrema*, known in Sanskrit as 'Karkatasringi' and in vernacular as 'Kakra Singi' is indigenous to India and belongs to the Natural Order, Anacardiaceae. It is commonly met with in sub-alpine Himalayas. On the leaves and petioles of this plant are found peculiar gall-like excrescences which give the appearance of horns from a distance, and hence the name 'Kakra Singi' of the plant. The galls have been regarded as highly medicinal in the Unani as well as in Ayurvedic system of medicines and are specially used as useful remedy in cough, phthisis, asthma and other ailments connected with lungs, heart and chest.

Chopra and Ghosh (*Ind. J. Med. Res.*, 1929, 17, 377) reported the presence of an essential oil (about 1.2%), a crystalline hydrocarbon (3.4%), tannins (60%) and gum mastic (5%) in the drug. They, however, did not examine the constituents of the essential oil.

The main fraction consisting of 94% of the total oil distilled at 154°-155° at atmospheric pressure. Analysis of the fraction was found to correspond with the composition of a terpene  $C_{10}H_{16}$ . It formed a nitrosochloride (m.p. 103°-104°) and nitrol piperide (m.p. 118°) and showed specific rotation of 32.6°. From the boiling point of the fraction, its analysis, melting points of the nitrosyl chloride and nitrol piperide and the optical activity, the terpene was identified as  $\alpha$ -d-pinene.

The constituents of the essential oils from the plants belonging to the N. O. of Anacardiaceae to which this plant belongs, invariably contain pinene as their chief component (cf. Parry, "Essential Oils", Vol. II, pp. 462, 463). Therefore, the discovery of pinene in the essential oil from *Pistacia integerrema* is in accordance with the feature characteristic of this family and it can be said in general that pinene is the chief component of the oils from plants belonging to this family. Read's view that botanical families can also be characterised by the chemical components of their essential oils is thus upheld.

### EXPERIMENTAL

*Isolation of the Essential Oil.*—The essential oil was obtained by steam-distillation of the dried galls of the plant from a copper still fitted with a spiral copper condenser. The oil separated from the steam distillate as a light greenish yellow layer which was removed and dried over anhydrous calcium chloride. The oil was obtained in 1.8% yield. It possesses the properties:  $d_{20}^{20}$ , 0.837;  $n_D^{20}$ , 1.474;  $[\alpha]_D^{21}$ , 36°; acid value, 4.5.

*Fractionation of the Oil.*—The oil (50 c.c.) on fractionation under reduced pressure (30 mm.) gave the following fractions:

- (I) 60°-61°, 47 c.c.
- (II) 95°-98°, 1.5 c.c.
- (III) Residue, 1.5 c.c.

*Identification of Pinene in Fraction (I).*—Fraction (I) distilled at 154°-155° at atmospheric pressure and showed indifference towards reagents for alcohols, aldehydes, acids and ketones, etc. It remained unaffected with 10% solution of caustic soda and absorbed much bromine. (Found: C, 88.1; H, 11.8.  $C_{10}H_{18}$  requires C, 88.2; 11.7 per cent).

*Formation of Nitrosyl Chloride.*—The fraction (I) (10 c.c.) was dissolved in glacial acetic acid (10 c.c.) and after cooling to 0°, amyl nitrite (20 c.c.) was added gradually, care being taken to keep the temperature low. After cooling the mixture thoroughly in ice and salt, hydrochloric acid (40 c.c., 2 parts acid and 1 part water) was added little by little. On standing a mass of light crystals separated, which were filtered off, dried and recrystallised from alcohol and ethyl acetate. The recrystallised nitrosyl chloride melted at 103-104°.

*Formation of Nitrol piperide.*—Nitrosochloride was dissolved in the least amount of alcohol and an alcoholic solution of piperidine was added to it and the mixture slightly warmed. The reaction product was poured in water when a solid white precipitate was obtained. It was filtered, dried and recrystallised from alcohol, m.p. 118°.

*Fraction (II).*—It distilled at 186°-189° at atmospheric pressure and absorbed bromine. It showed the reactions of an acid as well as an aldehyde. Thus it reduced ammoniacal silver nitrate and Fehling's solution, but did not form any semicarbazone. As the amount of the fraction was very small it could not be worked up further.

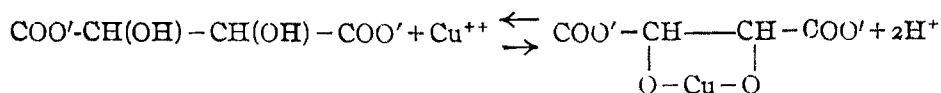
# METALLIC COMPLEXES OF TARTARIC AND CITRIC ACIDS. PART I. COPPER-TARTARIC ACID

By R. N. SEN SARMA

From conductometric and absorption measurements it has been shown that in dilute solution cupric ion forms with tartaric acid a complex containing the metal and tartrate in the proportion of 1:1. By utilising Job's method of continued variation the instability constant of the complex has been calculated and found to be  $1.21 \times 10^{-3}$ .

It is well known that the presence of tartaric acid or alkali tartrates interferes with the quantitative estimation of copper. The cause is attributed to the formation of a complex the exact nature of which is not definitely known, inspite of the considerable work which has been done. The object of the present investigation is to study the above reaction thoroughly from different physico-chemical standpoints. Conductometric and absorption measurements have been made to ascertain the course of the reaction, and by utilising Job's method of continued variation (*Compt. rend.*, 1925, 180, 928) the nature of the complex and the extent of its dissociation have been calculated.

Earlier work is confined to the isolation of compounds by fractional precipitation with alcohol from solution of copper tartrate dissolved in varying quantities of alkali (Masson and Steele, *J. Chem. Soc.*, 1899, 76, 725; Pickering, *ibid.*, 1910, 97, 1837; 1911, 99, 169, 1347; 1912, 101, 174; Packer and Warck, *ibid.*, 1921, 119, 1348; Warck, *ibid.*, 1923, 123, 1815, 1826; 1927, 1753). They isolated several compounds containing varying proportions of copper, tartrate and alkali metals. Dumansky and Chalisew (*Kolloid Z.*, 1928, 42, 121) have contended that they are not definite compounds but merely colloidal suspensions of cupric hydroxide in neutral or alkaline tartrate. From the physico-chemical standpoint the reaction was first studied by Jellinek and Gordon (*Z. physikal. Chem.*, 1924, 112, 207). From the e. m. f. measurements of an electrode of the metal in a tartrate solution of small hydrogen-ion concentration containing a small amount of the metal salt they concluded that in acid solution copper and tartrate ions reacted to form a complex in the proportion of 1:1.



Shinichiro and Hakomori (*Sci. Rep. Tôhoku Imp. Univ.*, 1927, 16, 841) supported this view from the study of the reaction of the metal in presence of tartaric acid by means of absorption spectrum, electrical conductivity, optical rotation, etc. in acid, neutral and ammoniacal medium. Recently Bobtelsky and Jordan (*J. Amer. Chem. Soc.*, 1945, 67, 1824) have studied the reaction by means of electrical conductivity and absorption and  $p_H$  measurements in dilute aqueous and 50% alcoholic solutions and have expressed the view that bivalent cations form

no complex with free acid but complexes are formed only with alkali tartrates in the ratio of 1:1. Unfortunately neither any data nor any graph in regard to the free acid are recorded.

From conductometric titration, measurements of electrical conductivity and absorption spectrum of solutions of copper nitrate and tartaric acid it has been definitely shown that the reaction occurs in the ratio of 1:1.

### EXPERIMENTAL

**Materials.**—Solutions prepared from Merck's copper nitrate, chloride and tartaric acid of reagent quality were used. For determination of purity both copper and tartaric acid were estimated iodometrically.

**Conductometric Measurements.**—All conductometric measurements were made by Philip's universal conductivity Bridge (model GM 4140) provided with 1000 cycle audio-frequency oscillator and magic eye. In conductometric titration copper nitrate solution was treated with tartaric acid and *vice versa*. The experimental data are plotted in Figs. 1 and 2. Besides conductometric titration, conductance measurements were made both in equimolecular and non-equimolecular solutions. Conductance was measured of each of the individual components as well as of their mixtures in varying proportions keeping the total volume constant. Tables I-II contain the

TABLE I

Conductivity experiment of  $M/10$ -copper nitrate with  $M/10$ -tartaric acid.  
Temp. =  $30^{\circ}$ . (Fig. 3, curve I).

Copper nitrate soln.	Water added.	Conduct. of the soln. in col. (1) $\times 10^4 = C_1$	Tartaric acid soln.	Water added.	Conduct. of the soln. in col. (3) $\times 10^4 = C_3$	$(C_1 + C_3) = C_2$	$M/10$ copper nitrate soln.	Tartaric acid soln. added.	Conduct. of the soln. in col. (6) $\times 10^4 = C_4$	$(C_1 - C_3) :$
1		2	3		4	5	6		7	8
50 c.c.	0 c.c.	264.6	0 c.c.	—	—	264.6	50 c.c.	0 c.c.	264.6	0
45	5	243.9	5	45 c.c.	16.1	260.0	45	5	281.7	21.7
40	10	217.4	10	40	24.4	241.8	40	10	270.3	28.5
35	15	195.3	15	35	30.3	225.6	35	15	259.7	34.1
33.3	16.7	186.0	16.7	33.3	32.0	218.0	33.3	16.7	253.2	35.2
32.5	17.5	181.8	17.5	32.5	32.8	214.6	32.5	17.5	250.0	35.4
30	20	170.9	20	30	35.1	206.0	30	20	242.4	36.4
27.5	22.5	158.7	22.5	27.5	37.7	196.4	27.5	22.5	233.9	37.5
25	25	146.0	25	25	40.0	186.0	25	25	224.7	38.7
22.5	27.5	133.0	27.5	22.5	41.8	174.8	22.5	27.5	211.9	37.1
20	30	119.5	30	20	43.9	163.4	20	30	198.8	35.4
17.5	32.5	106.4	32.5	17.5	45.9	152.3	17.5	32.5	185.5	33.2
16.7	33.3	101.0	33.3	16.7	46.5	147.5	16.7	33.3	180.2	32.7
15	35	93.5	35	15	47.6	141.1	15	35	172.4	31.3
10	40	64.5	40	10	51.0	115.5	10	40	140.3	24.8
5	45	33.3	45	5	54.1	87.4	5	45	103.1	15.7
—	—	—	50	0	56.2	56.2	0	50	56.2	0

experimental data of equimolecular and Tables III-V, those of non-equimolecular solutions respectively. In curves I-II (Fig. 3) and curves I-III (Fig. 4) the divergences from the additivity rule are plotted against the composition of the mixtures for equimolecular and non-equimolecular solutions respectively. In all measurements the reciprocal of the observed resistance, *i.e.* conductance being sufficient to draw the graph, the cell constant was not determined.

*Absorption Measurements.*—Absorption measurements were made by Lumetron Fluorescence meter (model 402 E. F.) of Photovolt Corporation. In this case also the absorption of both equimolecular and non-equimolecular solutions was measured. The experimental data are given in Tables VI-XI for equimolecular and in XII-XIV for non-equimolecular solutions respectively. In curves I-IV (Fig. 5) and I-II (Fig. 6) and I-III (Fig. 7) the divergences from the additivity rule are plotted against composition of the mixtures for equimolecular and non-equimolecular solutions respectively. In all the cases optical density has been plotted against composition of the mixture. Absorption due to complex formation and also of copper are in the same region (red). Wave-lengths 640, 660, 700 and 730m $\mu$  have been used for equimolecular and 700 and 730m $\mu$  for non-equimolecular solutions. All the measurements have been made at room temperature varying between 30° and 32°.

TABLE II

Conductivity experiment of *M/20-copper chloride with M/20-tartaric acid.*  
Temp. = 30°. (Fig. 3, curve II).

Copper chloride soln. Water added.		Conduct. of the soln. in col. (1) $\times 10^4 = C_1$	Tartaric acid soln. Water added.		Conduct. of the soln. in col. (3) $\times 10^4 = C_3$	$(C_1 + C_3) = C_2$	Copper chloride soln. Tartaric acid soln. added.		Conduct. of the soln. in col. (6) $\times 10^4 = C_4$	$(C_4 - C_2)$
1			3				6			
50 c.c.	0 c.c.	125.0	—	—	—	125.0	50 c.c.	0 c.c.	125.0	0
45	5	114.9	5 c.c.	45 c.c.	8.7	123.6	45	5	129.9	6.3
40	10	103.6	10	40	14.3	117.9	40	10	129.0	11.1
35	15	92.6	15	35	17.5	110.1	35	15	124.2	14.1
33.3	16.7	88.5	16.7	33.3	18.5	107.0	33.3	16.7	122.0	15.0
32.5	17.5	86.5	17.5	32.5	19.6	105.8	32.5	17.5	121.2	15.4
30	20	80.0	20	30	20.8	100.8	30	20	117.0	16.2
27.5	22.5	74.1	22.5	27.5	22.2	96.3	27.5	22.5	113.3	17.0
25	25	67.1	25	25	23.5	90.6	25	25	108.7	18.1
22.5	27.5	61.0	27.5	22.5	24.8	85.8	22.5	27.5	103.3	17.5
20	30	54.1	30	20	26.0	80.1	20.0	30.0	97.1	17.0
17.5	32.5	48.8	32.5	17.5	26.7	75.5	17.5	32.5	91.7	16.2
16.7	33.3	46.5	33.3	16.7	27.2	73.7	16.7	33.3	89.3	15.6
15	35	42.6	35	15	27.8	70.4	15	35	85.2	14.8
10	40	29.4	40	10	30.3	59.7	10	40	70.4	10.7
5	45	15.4	45	5	32.1	47.5	5	45	53.2	5.7
—	—	—	50	0	33.3	33.3	0	50	33.3	

TABLE III.

*Conductivity experiment of M/20-copper nitrate with M/5-tartaric acid.*

Temp. = 30°. (Fig. 4, curve I)

Copper nitrate soln.	Water added.	Conduct. of the soln. in col. (1) $\times 10^4 = C_1$ .	Tartaric acid soln.	Water added.	Conduct. of the soln. in col. (3) $\times 10^4 = C_3$ .	$(C_1 + C_3) = C_5$ .	Copper nitrate soln.	Tartaric acid soln. added.	Conduct. of the soln. in col. (6) $\times 10^4 = C_4$ .	$(C_4 - C_3)$ .
1		2		3	4	5	6		7	8
50 c.c.	0 c.c.	144.9	—	—	—	144.9	50 c.c.	0 c.c.	144.9	
45	5	136.1	5 c.c.	45 c.c.	24.7	160.8	45	5	190.5	29.7
40	10	120.5	10	40	36.5	157.0	40	10	194.6	37.6
37.5	12.5	114.3	12.5	37.5	41.2	155.5	37.5	12.5	194.2	38.7
36	14	111.1	14	36	43.5	154.6	36	14	193.4	38.8
35.5	14.5	109.5	14.5	35.5	44.4	153.9	35.5	14.5	193.2	39.5
35	15	108.3	15	35	45.1	153.4	35	15	192.3	38.9
32.5	17.5	101.0	17.5	32.5	49.3	150.3	32.5	17.5	188.3	38.0
30	20	94.3	20	30	52.1	146.4	30	20	183.5	37.1
25	25	80.0	25	25	58.8	138.8	25	25	173.0	34.2
20	30	64.5	30	20	64.5	129.0	20	30	160.0	31.0
15	35	50.5	35	15	69.9	120.4	15	35	144.9	24.5
10	40	34.5	40	10	75.2	109.7	10	40	126.6	16.9
—	—	—	50	0	84.8	84.8	—	50	84.8	0

TABLE IV

*Conductivity experiment of M/20-copper nitrate with M/10-tartaric acid.*

Temp. = 30°. (Fig. 4, curve II).

Copper nitrate soln.	Water added.	Conduct. of the soln. in col. (1) $\times 10^4 = C_1$ .	Tartaric acid soln.	Water added.	Conduct. of the soln. in col. (3) $\times 10^4 = C_3$ .	$(C_1 + C_3) = C_5$ .	Copper nitrate soln.	Tartaric acid soln. added.	Conduct. of the soln. in col. (6) $\times 10^4 = C_4$ .	$(C_4 - C_3)$ .
1		2		3	4	5	6		7	8
50 c.c.	0 c.c.	142.9	—	—	—	142.9	50 c.c.	0 c.c.	142.9	0
40	10	117.6	10 c.c.	40 c.c.	24.1	141.7.	40	10	165.3	23.6
35	15	104.2	15	35	30.3	134.5	35	15	162.1	27.6
32.5	17.5	98.0	17.5	32.5	32.8	130.8	32.5	17.5	159.5	28.7
30.5	19.5	91.7	19.5	30.5	34.5	126.2	30.5	19.5	155.5	29.3
30	20	90.5	20	30	35.0	125.5	30	20	155.0	29.5
29.5	20.5	89.0	20.5	29.5	35.6	124.6	29.5	20.5	153.8	29.2
27.5	22.5	83.3	22.5	27.5	37.2	120.5	27.5	22.5	149.3	28.8
25	25	77.5	25	25	39.5	117.0	25	25	143.9	26.9
22.5	27.5	70.4	27.5	22.5	41.7	112.1	22.5	27.5	137.4	25.3
20	30	63.7	30	20	43.9	107.6	20	30	131.1	23.5
15	35	49.3	35	15	47.6	96.9	15	35	116.6	19.7
10	40	33.9	40	10	51.9	84.9	10	40	99.0	14.1
—	—	—	50	0	56.2	56.2	0	50	56.2	0

TABLE V

*Conductivity experiment of M/30-copper nitrate with M/10-tartaric acid.*

Temp. = 30°. (Fig. 4, curve III).

Copper nitrate soln.	Water added.	Conduct. of the soln. in col. (1) $\times 10^4 = C_1$ .	Tartaric acid soln.	Water added.	Conduct. of the soln. in col. (3) $\times 10^4 = (C_2)$ .	$(C_1 + C_2) = C_3$ .	Copper nitrate soln.	Tartaric acid soln. added.	Conduct. of the soln. in col. (6) $\times 10^4 = C_4$ .	$(C_4 - C_3)$ .
1		2	3		4	5	6		7	8
50 c.c.	0 c.c.	105.8	—	—	—	105.8	50 c.c.	0 c.c.	105.8	0
40	10	87.7	10 c.c.	40 c.c.	25.3	113.0	40	10	132.5	19.5
37.5	12.5	82.0	12.5	37.5	28.6	110.6	37.5	12.5	131.6	21.0
35	15	76.3	15	35	31.8	108.1	35	15	130.7	22.6
32.5	17.5	72.4	17.5	32.5	34.1	106.5	32.5	17.5	129.9	23.4
32	18	71.2	18	32	34.5	105.7	32	18	129.4	23.7
31.5	18.5	69.9	18.5	31.5	34.8	104.7	31.5	18.5	128.2	23.5
30	20	67.1	20	30	36.9	104.0	30	20	126.6	22.6
27.5	22.5	62.5	22.5	27.5	39.2	101.7	27.5	22.5	123.5	21.8
25	25	57.1	25	25	41.5	98.6	25	25	119.0	20.4
20	30	45.9	30	20	46.1	92.0	20	30	118.7	16.7
15	35	35.7	35	15	49.8	85.5	15	35	99.0	13.5
10	40	24.4	40	10	53.2	77.6	10	40	86.2	8.6
—	—	—	50	0	58.4	58.4	0	50	58.4	0

TABLE VI

*Absorption measurement of M/50-copper nitrate with M/50-tartaric acid.*

(Fig. 5, curve 1)

Wave-length used = 730m $\mu$ .

Copper nitrate soln.	Tartaric acid soln.	Optical density of the soln. in col. (1) $\times 10^2 = (D_1)$	(Exptl.) optical density in case of no reaction $\times 10^2 = (D_2)$ .	$(D_1 - D_2) = D$ .
1		2	3	4
50 c.c.	0 c.c.	33.7	33.7	0
45	5	31.9	29.7	2.2
40	10	30.1	27.0	3.1
35	15	27.6	23.6	4.0
30	20	24.5	20.2	4.3
25	25	21.5	16.8	4.7
20	30	18.0	13.5	4.5
15	35	14.0	10.0	4.0
10	40	10.0	6.8	3.2
5	45	5.8	3.4	2.2
0	50	—	—	0

TABLE VII

*Absorption measurement of M/50-copper nitrate with M/50-tartaric acid.*

(Fig. 5, curve II)

Wave-length used = 700m $\mu$ .

Copper nitrate soln.	Tartaric acid soln.	Optical density of the soln. in col. (1) $\times 10^2 = (D_1)$ .	(Exptl.) optical density in case of no reaction $\times 10^2 = (D_2)$ .	$(D_1 - D_2) = D$ .
1		2	3	4
50 c.c.	0 c.c.	32.8	32.8	0
45	5	31.0	29.5	1.5
40	10	28.8	26.0	2.8
35	15	26.8	23.0	3.8
30	20	23.7	19.7	4.0
25	25	20.8	16.4	4.4
20	30	17.4	13.1	4.3
15	35	13.8	9.8	3.7
10	40	9.2	6.5	2.7
5	45	5.1	3.3	1.8
0	50	—	—	0

TABLE VIII

*Absorption measurement of M/50-copper nitrate with M/50-tartaric acid.*

(Fig. 5, curve III)

Wave-length used = 660m $\mu$ .

Copper nitrate soln.	Tartaric acid soln.	Optical density of the soln. in col. (1) $\times 10^2 = (D_1)$ .	(Exptl.) optical density in case of no reaction $\times 10^2 = (D_2)$ .	$(D_1 - D_2) = D$ .
(1)		(2)	(3)	(4)
50 c.c.	0 c.c.	17.1	17.1	0
45	5	16.0	15.4	0.6
40	10	14.9	13.7	1.2
35	15	13.5	12.0	1.5
30	20	12.0	10.0	2.0
25	25	10.8	8.5	2.3
20	30	9.0	6.9	2.1
15	35	6.8	5.1	1.7
10	40	4.5	3.3	1.1
5	45	2.2	1.7	0.5
0	50	—	—	0



TABLE IX

*Absorption measurement of M/50-copper nitrate with M/50-tartaric acid.*

(Fig. 5, curve IV)

Wave-length used = 640m $\mu$ .

Copper nitrate soln.	Tartaric acid soln.	Optical density of the soln. in col. (1) $\times 10^3 = (D_1)$ .	(Exptl.) optical density in case of no reaction $\times 10^3 = (D_2)$ .	$(D_1 - D_2) = D$ .
(1)		(2)	(3)	(4)
50 c.c.	0 c.c.	12.5	12.5	0
45	5	11.9	11.5	0.4
40	10	11.2	10.2	1.0
35	15	10.2	8.8	1.4
30	20	9.3	7.5	1.8
25	25	8.3	6.2	2.1
20	30	6.8	5.0	1.8
15	35	5.1	3.8	1.3
10	40	3.2	2.5	0.7
5	45	1.4	1.2	0.2
0	50	—	—	0

TABLE X

*Absorption measurement of M/30-copper nitrate with M/30-tartaric acid.*

(Fig. 6, curve I)

Wave-length used = 700m $\mu$ .

Copper nitrate soln.	Tartaric acid soln.	Optical density of the soln. in col. (1) $\times 10^3 = (D_1)$ .	(Exptl.) optical density in case of no reaction $\times 10^3 = (D_2)$ .	$(D_1 - D_2) = D$ .
(1)		(2)	(3)	(4)
50 c.c.	0 c.c.	53.7	53.7	0
40	10	48.2	43.2	5.0
35	15	44.4	38.0	6.4
30	20	41.0	32.6	8.4
27.5	22.5	39.0	29.8	9.2
25	25	36.7	27.0	9.7
22.5	27.5	33.0	24.0	9.0
20	30	29.7	21.6	8.1
15	35	22.6	16.2	6.4
10	40	16.1	10.8	5.3
5	50	—	—	0

TABLE XI

*Absorption measurement M/40-copper nitrate with M/40-tartaric acid.*

(Fig. 6, curve II)

Wave-length used = 730m $\mu$ .

Copper nitrate soln.	Tartaric acid soln.	Optical density of the soln. in col. (1) $\times 10^2 = (D_1)$ .	(Exptl.) optical density in case of no reaction $\times 10^2 = (D_2)$ .	$(D_1 - D_2) = D$ .
(1)		(2)	(3)	(4)
50 c.c.	0 c.c.	42.5	42.5	0
40	10	38.2	34.0	4.2
35	15	35.2	29.8	5.4
30	20	31.9	25.5	6.4
27.5	22.5	30.1	23.5	6.6
25	25	28.4	21.3	7.1
22.5	27.5	26.0	19.2	6.8
20	30	23.2	17.0	6.2
15	35	18.4	12.8	5.6
10	40	13.0	8.5	4.5
0	50	—	—	0

TABLE XII

*Absorption measurement of M/50-copper nitrate with M/10-tartaric acid.*

(Fig. 7, curve I)

Wave-length used = 730m $\mu$ .

Copper nitrate soln.	Tartaric acid soln.	Optical density of the soln. in col. (1) $\times 10^2 = (D_1)$ .	(Exptl.) optical density in case of no reaction $\times 10^2 = (D_2)$ .	$(D_1 - D_2) = D$ .
(1)		(2)	(3)	(4)
50 c.c.	0 c.c.	33.7	33.7	0
40	10	34.2	26.8	7.4
37.5	12.5	33.3	25.1	8.2
35	15	32.3	23.5	8.8
33.5	16.5	31.9	22.6	9.3
32.5	17.5	30.8	21.8	9.0
30	20	28.8	20.1	8.7
25	25	25.2	16.8	8.4
20	30	21.5	13.5	8.0
10	40	12.8	6.8	6.0
0	50	—	—	0

TABLE XIII

*Absorption measurement of M/50-copper nitrate with M/10-tartaric acid.*

(Fig. 7, curve II)

Wave-length used = 700m $\mu$ .

Copper nitrate soln.	Tartaric acid soln.	Optical density of the soln. in col. (1) $\times 10^2 = (D_1)$ .	(Exptl.) optical density in case of no reaction $\times 10^2 = (D_2)$ .	$(D_1 - D_2) = D$ .
(1)		(2)	(3)	(4)
50 c.c.	0 c.c.	32.8	32.8	0
40	10	33.3	26.0	7.3
37.5	12.5	32.3	24.5	7.8
35	15	31.5	22.8	8.7
33.5	16.5	31.0	21.8	9.2
32.5	17.5	29.9	21.1	8.8
30	20	28.0	19.5	8.5
25	25	24.4	16.3	8.1
20	30	20.4	13.0	7.4
10	40	12.0	6.6	5.4
0	50	—	—	—

TABLE XIV

*Absorption measurement of M/40-copper nitrate with M/10-tartaric acid.*

(Fig. 7, curve III)

Wave-length used = 730m $\mu$ .

Copper nitrate soln.	Tartaric acid soln.	Optical density of the soln. in col. (1) $\times 10^2 = (D_1)$ .	(Exptl.) optical density in case of no reaction $\times 10^2 = (D_2)$ .	$(D_1 - D_2) = D$ .
(1)		(2)	(3)	(4)
50 c.c.	0 c.c.	42.5	42.5	0
40	10	42.0	33.7	8.3
35	15	40.0	29.5	10.5
32.5	17.5	38.7	27.5	11.2
30	20	36.2	25.5	10.7
27.5	22.5	33.7	23.5	10.2
25	25	31.0	21.3	9.7
20	30	26.0	17.0	9.0
10	40	14.3	8.0	6.3
0	50	—	—	0

## DISCUSSION

It will be seen that the conductometric titration curves (Fig. 1 and 2) are almost continuous, although a slight break can be noticed when the ratio of the reactants is 1:1. It cannot therefore be definitely concluded that the reaction occurs in that

FIG. 1

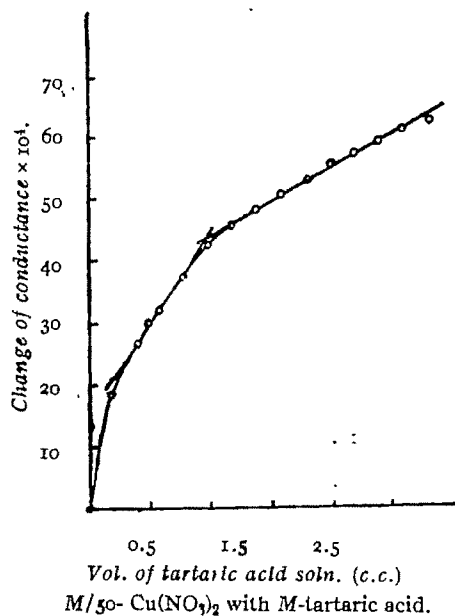


FIG. 2

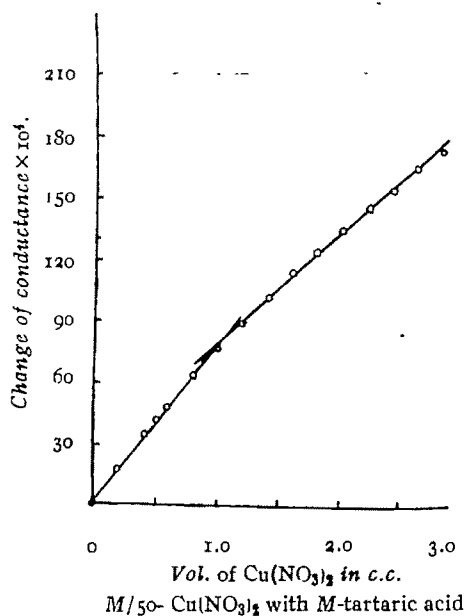
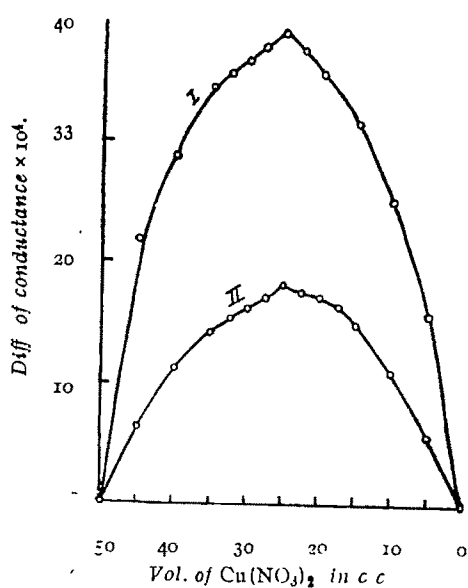
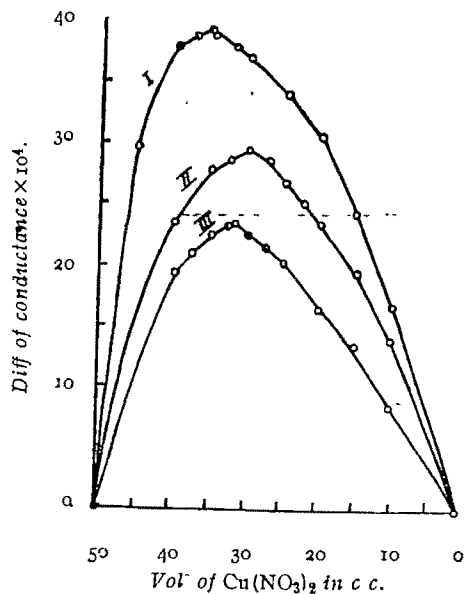


FIG. 3



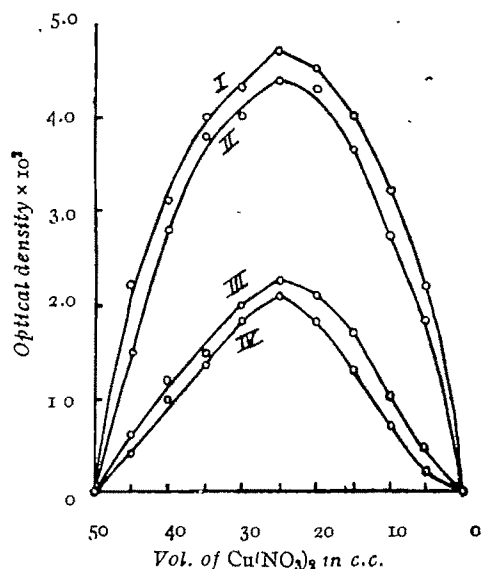
Curves I and II represent respectively  
 M/10- $\text{Cu}(\text{NO}_3)_2$  + M/10- tartaric acid and  
 M/20- $\text{CuCl}_2$  + M/20- tartaric acid.

FIG. 4



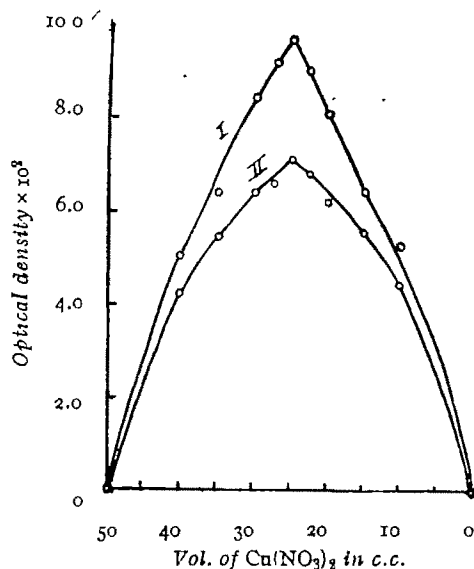
I—M/20-  $\text{Cu}(\text{NO}_3)_2$  + M/5- tartaric acid  
 II— " " + M/10- "  
 III—M/30 " + " "

FIG. 5



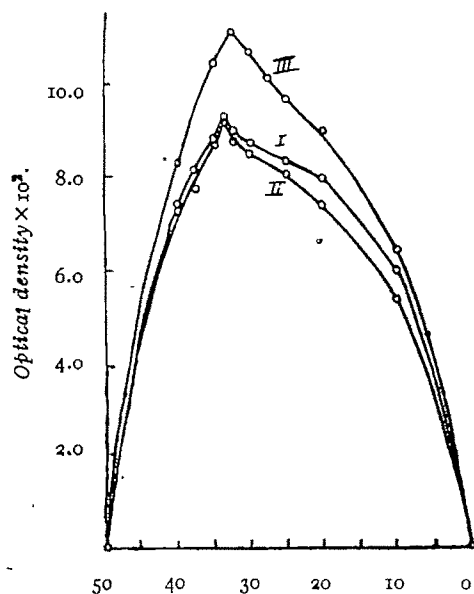
I-IV refer to  $M/50$ -  $\text{Cu}(\text{NO}_3)_2 + M/50$ - tartaric acid in 730, 700, 660 and 640 mμ respectively.

FIG. 6



Curves I and II represent respectively  $M/30$ -  $\text{Cu}(\text{NO}_3)_2 + M/30$ -tartaric acid in 700 mμ and  $M/40$ -  $\text{Cu}(\text{NO}_3)_2 + M/40$ - tartaric acid in 730 mμ.

FIG. 7



I-II represent  $M/50$ -  $\text{Cu}(\text{NO}_3)_2 + M/10$ - tartaric acid respectively to 730, 700 mμ and III represents  $M/40$ -  $\text{Cu}(\text{NO}_3)_2 + M/10$ - tartaric acid in 730 mμ.

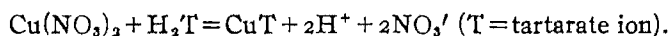
proportion. The continuous nature of the curves may be due to the fact that the complex is less stable in acid medium and the statement of Bobtelsky and Jordan (*loc. cit.*) that the free acid forms no complex is perhaps due to the same cause.

The conductance measurements leads definitely to the conclusion that the reaction occurs when the ratio of the reactants is 1:1. It will be observed that in equimolecular solutions a maximum is obtained at that ratio, when the divergence from the additivity rule due to complex formation is plotted against composition (Fig. 3, curves I-II). The experimental data show that the observed conductance of the mixture is greater than the sum of the conductance of the individual components. The increase in conductance can only be attributed to the liberation of highly mobile hydrogen ion from tartaric acid molecule as a result of

reaction between the salt and the acid.

Measurement of absorption of equimolecular solution in different wave-lengths also supports the conclusion of<sup>3</sup> the conductance measurements (Fig. 5, curve I-IV ; Fig. 6, curves I-II).

The experimental results leave no doubt that in dilute solutions only one complex is formed between cupric ion and free tartaric acid in the ratio of 1:1. The reaction occurs probably as follows :



Now by applying Job's method of continued variation the instability constant can be calculated from the measurements of conductance and absorption in non-equimolecular solutions.

The equation relating to the value of  $K$ , the instability constant, is given by,

$$K = \frac{C\{(p+1)x-1\}^2}{(p-1)(1-2x)},$$

where  $C$  is the molar concentration of copper nitrate,  $p$ , the molar concentration of tartaric acid,  $x$ , c.c. of tartaric acid combining with  $(1-x)$  c.c. of copper nitrate to give the maximum effect.

TABLE XV

*Conductometric measurement.*

Table No	Fig. No.	Curve No.	$C$	$p$ .	$x$ .	$K \times 10^3$ .	Mean $K \times 10^3$ .
V	4	I	0.05	4	0.29	0.80	
VI	4	II	0.05	2	0.40	1.00	0.96
VII	4	III	0.033	3	0.36	1.00	

TABLE XVI

*Absorption measurement.*

Table No.	Fig. No.	Curve No.	Wave-length.	$C$ .	$p$ .	$x$ .	$K \times 10^3$ .	Mean $K \times 10^3$ .
XII	7	I	730m $\mu$	0.02	5	0.33	1.43	
XIII	7	II	700	0.02	5	0.33	1.43	1.47
XIV	7	III	730	0.025	4	0.35	1.57	

The mean value of  $K$  obtained from the two methods is  $1.21 \times 10^{-2}$ .

Further work with alkali tartrate is in progress.

In conclusion the author wishes to express his best thanks to Dr. P. B. Sarkar, Ghose Professor of Chemistry, University College of Science and Technology, Calcutta for valuable and helpful discussion, to Prof. H. L. Roy and Prof. A. K. Majumdar of the Chemical Engineering Department, College of Engineering & Technology, Jadavpur, for their interest.

INORGANIC CHEMISTRY LABORATORIES,  
CHEMICAL ENGINEERING DEPARTMENT,  
COLLEGE OF ENGINEERING & TECHNOLOGY,  
JADAVPUR, BENGAL.

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## SEARCH FOR NEW ANTISPASMODICS. PART II.

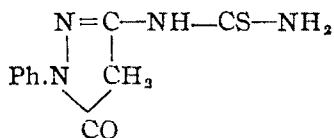
BY T. N. GHOSH

Synthesis of a thiazylpyrazolone derivative (II) and the corresponding methylene-bis compound (III) is described.

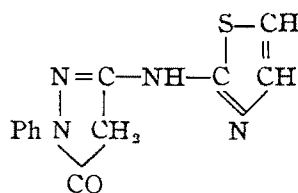
Following the observation of Notkin and Webster (*Rev. Canadian Biol*, 1942, 1, 660) that amidopyrine, which is a pyrazolone derivative, possesses antispasmodic activity, the synthesis of some pyrazolone derivatives containing tertiary bases has been described in part I (Pathak and Ghosh, this *Journal*, 1949, 26, 371). Investigation is in progress to see if these compounds have any broncho-dilator effect.

Heilbron and his co-workers (*J. Chem. Soc.*, 1943, 419) have synthesised a number of pyridylquinoline and thiazylquinoline derivatives, some of which have been found to possess pronounced antispasmodic action with the promise of useful additions to the range of drugs suitable for treating asthmatic and other conditions. In view of these observations, it has been considered desirable to synthesise thiazylpyrazolone derivatives as possible antispasmodics.

The hydrochloride of 1-phenyl-3-amino-5-pyrazolone (Weissberger and Porter, *J. Amer. Chem. Soc.*, 1942, 64, 2133) has now been allowed to react with potassium thiocyanate to yield the corresponding thiocarbamide derivative (I). When (I) is reacted with  $\alpha\beta$ -dichlorodiethyl ether, the thiazylpyrazolone derivative (II) is obtained.

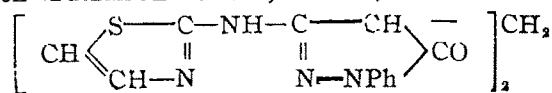


(I)



(II)

A survey of the chemistry of efficient antispasmodics shows that they are, in general, salts of tertiary bases. In order to enhance the antispasmodic activity, it has been considered worth while to introduce tertiary bases into the above compound (II). Compounds other than ketones, but containing an active methyl or methylene group, may sometimes be induced to respond to Mannich reaction (cf. Kermack and Muir, *J. Chem. Soc.*, 1931, 3089; Pathak and Ghosh, *loc. cit.*). As the compound (II) contains a reactive methylene group, it was substituted for the ketone in the usual Mannich reaction which, however, when attempted with piperidine hydrochloride and formaldehyde, did not yield the expected tertiary base but furnished the methylene-bis compound (III). In this respect the above pyrazolone derivative (II) behaves differently from 1-phenyl-3-methylpyrazolone or its 4-acetyl derivative, both of which respond to Mannich reaction (Pathak and Ghosh, *loc. cit.*).



(III)

In this connection, reference is made to the formation of methylene-bis-antipyrine, when antipyrine is employed for the usual Mannich reaction (cf. Lieberman and Wagner, *J. Org. Chem.*, 1949, **14**, 1008).

#### EXPERIMENTAL

**1-Phenyl-3-thiocarbamido 5-pyrazolone (I).**—1-Phenyl-3-amino-5-pyrazolone was prepared according to the method of Conrad and Zart (*Ber.*, 1906, **39**, 2282), as modified by Armstrong (*J. Amer. Chem. Soc.*, 1942, **64**, 2134, footnote). The alcohol used should be absolute, otherwise the presence of traces of moisture lowers the yield considerably.

The above amino compound (8.8 g.) was dissolved in just the requisite quantity of dilute hydrochloric acid and to the clear solution a concentrated aqueous solution of potassium thiocyanate (6.2 g.) was added, when a heavy oil was obtained. The mixture was then heated on the wire-gauge for about 20 minutes and then allowed to cool. The solid obtained was crystallised from alcohol in light yellow rectangular plates (7.5 g.), shrinking at 190° and decomposing at 198-99°. It is readily soluble in cold dilute alkali and precipitated by excess of dilute hydrochloric acid. It is desulphurised when an alcoholic solution is boiled with yellow oxide of mercury. It was dried at 95°-100° in *vacuo*. (Found: N, 23.72.  $C_{10}H_{10}ON_4S$  requires N, 23.93 per cent).

**1-Phenyl-3-(thiazyl-2'-) amino-5-pyrazolone (II).**—To a hot alcoholic solution of the compound (I, 7.5 g.)  $\alpha\beta$ -dichlorodiethyl ether (5 g.) was gradually added, and the solution was heated on the water-bath under reflux for 2 hours, when it turned red. The solution was diluted sufficiently with water and the mixture was heated on the water-bath for one hour more. The pasty mass, thus obtained, was purified by solution in cold dilute alkali and precipitation by dilute hydrochloric acid. The solid obtained was crystallised from alcohol in reddish brown needles (5.2 g.), m.p. 220-21° (decomp.) It was dried in *vacuo* at 110°-115°. (Found: N, 21.38.  $C_{12}H_{10}ON_4S$  requires N, 21.70 per cent). The compound is not desulphurised by yellow oxide of mercury, proving the presence of sulphur in the ring and the formation of thiazole derivative.

**Methylene-bis-[1-phenyl-3-(thiazyl-2'-) amino-5-pyrazolone] (III).**—A mixture of the above compound (II, 7.7 g.), piperidine (3.8 g.), hydrochloric acid (8.1 c.c., 20% w/v) and formaldehyde (3.4 c.c., 40%) in alcohol (75 c.c.) was heated under reflux on the water-bath for 8 hours. Next day alcohol was distilled under reduced pressure. The residue was treated with water, filtered and found to be not a hydrochloride. It was purified by treating successively with cold caustic soda solution (1%) and with dilute hydrochloric acid, in both of which it was practically insoluble. It was finally crystallised from alcohol in brownish needles, m.p. 259-60°. (Found: N, 20.86.  $C_{22}H_{20}O_2N_8S_2$  requires N, 21.21 per cent).

The above reaction was carried out in absence of hydrochloric acid (compare Lieberman and Wagner, *loc.cit.*), first at room temperature for 12 hours and afterwards by heating on the water-bath under reflux for 6 hours. Under these conditions also, only the above compound (III) could be isolated.



## ANALYTICAL CHEMISTRY OF THORIUM. PART I. SEPARATION FROM CERITE EARTHS WITH *o*-CHLOROBENZOIC ACID

BY B.R. LAKSHMANA RAO AND BH. S.V. RAGHAVA RAO

Thorium is precipitated quantitatively by *o*-chlorobenzoic acid from solutions of  $p_H$  2.8 and the above separation from rare earths may be accomplished by a single precipitation from solutions just neutral to Congo red; U, Ni Co, Al and Pb in moderate amounts do not interfere.

Several methods are available for the estimation of thorium, but its separation from the associated cerite earths in monazite is still a problem of some complexity. For the effective removal of the rare earths all reagents require a double precipitation. The following procedure with *o*-chlorobenzoic acid will be of interest both on account of its simplicity and effectiveness. Working with artificial mixtures of thoria and ceria it has been noticed that a sharp separation of thorium results by a single precipitation even in the presence of a ten-fold excess of ceria. When it is taken into account that on the average the ratio of  $\text{ThO}_2$  to  $\text{R}_2\text{O}_3$  is 1 : 12 (and in Indian monazite particularly this ratio is not more than 1 : 8), the advantage offered by this reagent in the recovery of thorium from monazite becomes more apparent.

### EXPERIMENTAL

**Estimation.**—A stock solution of pure thorium nitrate was prepared and estimated with *m*-nitrobenzoic acid (Neish, *Chem. News*, 1904, 90, 196). 10 ml. of the solution gave 0.0748 g. of  $\text{ThO}_2$ . The same was determined with *o*-chlorobenzoic acid, by precipitating with 0.75 g. of the reagent in boiling solution and igniting the precipitate found 0.0749 g. in excellent agreement with the standard procedure.

**Separation.**—In as much as separation from other rare earths rests on preferential precipitation under controlled  $p_H$ , the precipitation of thorium under different conditions of  $p_H$  was investigated. It was noticed that the precipitation of thorium was not complete when the  $p_H$  was lower than 2.8, and at  $p_H$  3.8 other rare earths started to precipitate. A convenient  $p_H$  range thus appeared to lie between 2.8 and 3.8, a condition that was easily realised by making the liquid just neutral to Congo red.

**Procedure.**—To the mixed solution containing not more than 0.150 g. of thoria and 1.5 g. of ceria add a few drops of Congo red and diluted ammonia dropwise until the liquid just reacts neutral. Dilute to 100 ml. and boil. Add with continuous stirring 0.75 g. of *o*-chlorobenzoic acid in 75 ml. of boiling water. Continue to boil for 3 minutes and set aside for 30 minutes. Collect the white flocculent precipitate on an 11 cm. Whatman No. 41 filter, wash first with 0.05% solution of the acid and finally with water. Ignite and weigh as  $\text{ThO}_2$ .

Results obtained with this procedure on thoria-ceria mixtures as well as other common elements are shown in Table I. The nitrates added are calculated to oxides.

TABLE I

*Separation of thorium from the cerite earths.*

(A). Amount of $\text{ThO}_2$ taken = 0.1496 g.			(B). Amount of $\text{ThO}_2$ taken = 0.0748 g.			
$\text{R}_2\text{O}_3$ added.	$\text{ThO}_2$ found.	Difference.	Admixture.	Quantity.	$\text{ThO}_2$ obtained.	Difference.
0.1200 g.	0.1496 g.	0 g.	$\text{R}_2\text{O}_3$	0.1200 g.	0.0747 g.	-0.0001 g.
0.2400	0.1498	+0.0002	,,	0.2400	0.0748	-0.0000
0.6000	0.1494	-0.0002	,,	0.6000	0.0747	-0.0001
1.2000	0.1496	0	,,	1.2000	0.0749	+0.0001
1.4000	0.1492	-0.0004	$\text{U}_3\text{O}_8$	0.1200	0.0746	-0.0002
			,,	0.2400	0.0748	+0.0000
			NiO	0.1000	0.0747	-0.0001
			CoO	0.1000	0.0746	-0.0002
			$\text{Al}_2\text{O}_3$	0.1000	0.0748	+0.0000
			PbO	0.1000	0.0749	+0.0001

Copper, titanium, iron and cerium (quadrivalent) interfere in the precipitation of thorium. Other elements have not been investigated nor are they likely to occur with this element.

*Composition of the Precipitate.*—From ignition tests on thorium chlorobenzoate it appears that each thorium ion is associated with three molecules of the acid besides four molecules of water. This indicates the presence of a hydroxyl group. The composition is subject to slight variations and therefore direct weighing of the precipitate is ruled out.

*Estimation of Thorium in Monazite.*—Accurately weighed quantities of Travancore monazite were digested with 3 to 4 times its weight of concentrated sulphuric acid for 4 hours at  $200^\circ$ - $250^\circ$ . The mass was extracted with ice cold water. The residue which was small consisted entirely of silica, titania and possibly zirconia. The oxalates of thorium and rare earths were precipitated twice with oxalic acid. The final oxalate precipitate, which was free from phosphoric acid, was dissolved in fuming nitric acid and evaporated to dryness. The residue was dissolved in water and the thorium was estimated with *o*-chlorobenzoic acid according to the procedure detailed above, as also with *m*-nitrobenzoic acid after a double precipitation.

<i>m</i> -Nitrobenzoic acid.		<i>o</i> -Chlorobenzoic acid.	
Sample.	$\text{ThO}_2$ (g.).	Sample.	$\text{ThO}_2$ (g.).
1.2540 g.	8.98%	1.3460 g.	9.03%
1.0240	9.00	1.0650	9.00
	Av. 8.99%	1.2142	9.02
			Av. 9.02%

## ANALYTICAL CHEMISTRY OF THORIUM. PART II. SEPARATION FROM CERITE EARTHS. *o*-AND *p*-AMINOBENZOIC ACIDS

By D. S. N. MURTHY AND BH. S. V. RAGHAVA RAO

Thorium can be precipitated quantitatively by *o*- and *p*-aminobenzoic acids from solutions of  $p_H$  4.2 and more. Rare earths in monazite can be removed by a double precipitation at the same  $p_H$ . Interference from other common elements is less in the case of *para*-acid.

In the course of an extended investigation into reagents suitable for the estimation and separation of thorium from rare earths in monazite we have noticed that both *o*- and *p*-aminobenzoic acids possess valuable properties (this *Journal*, 1949, 26, 487). Sodium anthranilate has been employed by Goto (*J. Chem. Soc. Japan*, 1934, 55, 1156) for the precipitation of Zn, Cd, etc., while the ammonium salt has been reported by Shemyakin and Belkon (*Compt. rend. Acad. Sci. U.S.S.R.*, 1938, 18, 275; *Chem. Abst.*, 1938, 32, 4470) to give an abundant dark red precipitate with tetravalent cerium. Both *o*- and *p*-aminobenzoic acids give voluminous precipitates with thorium, and as small as 1.0 mg. of thorium gives a precipitate sufficient for convenient handling. The *para*-benzoate is more fine and has a greater tendency to become colloidal, but it has the advantage that interference from other metals is much less.

### EXPERIMENTAL

*Estimation.*—A stock solution of pure thorium nitrate was estimated with *m*-nitrobenzoic acid (Neish, *Chem. News*, 1904, 90, 196). 20 ml. of this solution gave 0.1498 g. of  $ThO_2$ . The same was determined with *o*- and *p*-benzoic acids by precipitation from boiling solution in the presence of ammonium acetate yielding the values 0.1496 g. and 0.1498 g. respectively in good agreement therewith.

*Separation of Thorium.*—Thorium is completely precipitated by both the acids at a  $p_H$  of 4.2 and over. Precipitation of other rare earths by these acids occurs at  $p_H$  4.8.

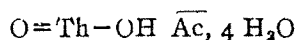
A convenient  $p_H$  for the effective removal of the rare earths will be 4.2 to 4.4 which is easily established under the following conditions.

(a) *Single Precipitation: Procedure.*—Make the solution just acid to Congo red and dilute to 10 ml. Add now 5 ml. of 5% ammonium acetate. Boil and add in a steady stream with continuous stirring 75 ml. of a boiling 1% solution of the reagent; continue to boil for 3 minutes, and set aside to cool. Collect the precipitate on Whatmann No. 41 (42 in case of *p*-acid) and wash with 0.1% solution of the precipitant. (Add 1 g. of ammonium acetate for every 250 ml. of wash liquid in the case *p*-acid). Dry, ignite and weigh as  $ThO_2$ .

(b) *Double Precipitation.*—When the rare-earth : thorium ratio is greater than 4 : 1, procedure will be as follows. Dissolve the precipitate in hot dilute nitric acid, catching the liquid in the original beaker. Adjust the acidity by adding carefully dilute ammonia

and ammonium acetate and repeat the precipitation. Wash, dry and ignite. Results obtained by this procedure are shown in Table I.

*Composition of the Precipitate.*—It is very interesting to note that the composition of the precipitate is not the same in both cases. While the anthranilates of divalent elements Zn, Cd, etc., are definite compounds and non-hydrated, the thorium compound is different. Ignition tests indicate that thorium anthranilate is anhydrous and in the precipitate two molecules of the acid are associated with one thorium ion, thus pointing to the presence of two hydroxyl groups. Thorium *p*-aminobenzoate on the other hand appears to have a composition in which one acid group is associated with one thorium ion together with 4 molecules of water. This salt then has the probable composition,



where Ac represents the acid group. The composition is not definite in both cases and shows slight variations. Ignition to the oxide is therefore necessary.

TABLE I

*Separation of thorium from rare earths.*

ThO<sub>2</sub> taken = 0.1498 g.

Admixture		<i>o</i> -Aminobenzoic acid.		<i>p</i> -Aminobenzoic acid.	
Cerite earths.		ThO <sub>2</sub> found.	Difference.	ThO <sub>2</sub> found.	Difference.
R <sub>2</sub> O <sub>3</sub>	0.189 g.	0.1496 g.	-0.2 mg.	0.1495 g.	-0.3 mg.
"	0.30	0.1495	-0.3	0.1497	-0.1
"	0.60	0.1496	-0.2	...	...
"	0.72	0.1497	-0.1	0.1498	0.0
"	1.20	0.1510 <sup>†</sup>	+1.2	0.1508*	+1.0
"	"	0.1498†	0.0	0.1497†	-0.1
"	1.40	0.1520*	+2.2	0.1519†	+2.1
"	"	0.1497†	-0.1	0.1496†	-0.2
"	1.80	0.1528*	+3.0	0.1530 <sup>†</sup>	+3.2
"	"	0.1495†	-0.3	0.1494†	-0.4

\* Single precipitation.

† Double precipitation.

#### *Interferences*

(a) *o*-Aminobenzoic acid.—Zr, Ti, Pb, Fe, Ce<sup>IV</sup>, Al, Cu, Ni, Co., UO<sub>2</sub><sup>++</sup> and Mn all gave high values of ThO<sub>2</sub> and the impurity persisted even after double precipitation.

(b) *p*-Aminobenzoic acid.—With this reagent there was no interference from a number of common elements viz., Pb, UO<sub>2</sub><sup>++</sup>, Co, Ni, Bi and Mn but Zr, Ce<sup>IV</sup>, Ti, Cu, and Al co-precipitated and even a double precipitation was not satisfactory. The amount

of impurity added amounted to 0.2 to 0.8 g. calculated to the oxide in every case. In all cases of interference its effect is noticeable even in amounts as small as 0.01 g.

*Estimation of Thorium in Monazite.*—The method was applied to the assay of monazite for thorium. The thorium was determined by double precipitation and the values were compared with those obtained with *m*-nitrobenzoic acid (*loc. cit.*). The decomposition of monazite (a sample from Travancore) has been described in an earlier communication (*vide* Part I, this *Journal*, 1950, 27, 457).

TABLE II

<i>m</i> -Nitrobenzoic acid.		<i>o</i> -Aminobenzoic acid.		<i>p</i> -Aminobenzoic acid.	
Sample.	ThO <sub>2</sub> .	Sample.	ThO <sub>2</sub> .	Sample.	ThO <sub>2</sub> .
1. 1.0869 g.	8.96%	1. 1.2849 g.	9.00%	1. 1.3054	8.97%
1. 1.2964 g.	9.00	2. 1.6475	8.98	2. 1.0240	8.96
3.		3. 1.7264	8.97	3. 1.5620	8.96
	Mean 8.98		Mean 8.98		Mean 8.97

CHEMICAL LABORATORY,  
ANDHRA UNIVERSITY,  
WALTAIR.

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## ON CERTAIN KETO-SULPHONES

BY U. P. BASU AND ACHINTYA KAMAL SEN

Certain keto-sulphones have been prepared and their properties studied.

Search for simple sulphones was undertaken in this laboratory since 1945 (cf. Sikdar and Basu, this *Journal*, 1945, 22, 343; Sikdar, *ibid.*, 1946, 23, 203; Basu and Chandran, *Science & Culture*, 1949, 15, 34) in the belief that they may exert a chemotherapeutic action against pulmonary tuberculosis (cf. Bambas, *J. Amer. Chem. Soc.*, 1945, 67, 668, 671). Many natural antibiotics again contain an  $\alpha\beta$ -unsaturated ketonic chain (cf. Basu, *Science & Culture*, 1948, 14, 191); and Rinderknecht *et al* (*Biochem. J.*, 1948, 41, 191) have made a systematic study on the nature of such chains and their relative activity against various pathogenic organisms. It is known that an  $\alpha\beta$ -unsaturated ketone readily reacts with benzenesulphinic acid (Kohler and Reimer, *Amer. Chem. J.*, 1904, 31, 163). Accordingly it was considered to be of interest to find out the activity of 4-aminophenylsulphones that might be easily obtained by condensing *p*-aminobenzenesulphinic acid with  $\alpha\beta$ -unsaturated ketones. While the work was just in progress we came across a patent literature (Ind. Pat., 33544) where certain keto-sulphones were described. They are being found to be active against coliform organisms. As our intention was to work on some products that might be effective against *M. tuberculosis*, some unsaturated ketones containing salicylidene, cinnamylidene group, and similar other aromatic aldehydes were obtained by condensing the aldehydes with appropriate ketone and the resulting unsaturated ketones were condensed with *p*-acetylaminobenzenesulphinic acid, and in certain cases with free *p*-aminobenzenesulphinic acid. In general, it is difficult to isolate the latter condensation products directly by hydrolysing the reaction products between the unsaturated ketones and the *p*-acetylaminobenzenesulphinic acid.

### EXPERIMENTAL

*General Method of Preparation.*—*p*-Acetaminobenzenesulphinic acid (1 mol.) was refluxed with the respective unsaturated compound (1 mol.) in alcoholic medium for 1-2 hours. The reaction mixture was cooled when the crystals separated which were filtered off, washed and recrystallised from alcohol. In the case of compound (V), chloroform-alcohol mixture was used for recrystallisation. The compounds that have been prepared and studied are listed in Table I.

The acetyl compound, when refluxed with 25 c.c. of caustic soda solution (10%) for two hours, underwent hydrolysis, but it was difficult to isolate the free compounds in good and pure quality. The free compounds, *para*-aminophenylsulphone derivatives were, however, prepared by refluxing molar amounts of *p*-aminobenzenesulphinic acid and the corresponding  $\alpha\beta$ -unsaturated ketones for 2 to 5 hours in alcoholic solution. On cooling, crystals separated out and they were recrystallised from alcohol. The detailed characteristics are recorded in Table II.

TABLE I



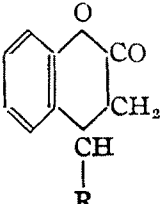
No.	Compound.	General appearance and melting point.	Formula and M W.	Percentage nitrogen.	
				Found.	Calc.
I.	$R.CH[C_6H_4.OH(o)]CH_2CO.Me$ <i>p</i> -Acetaminophenyl (1- <i>o</i> -hydroxyphenyl-2-acetylethyl) sulphone	White crystals, m.p. 173-74°	$C_{18}H_{19}O_5NS$ (361)	4.34	3.88
II.	$R.CH[C_6H_4.OH(p)]CH_2CO.Me$ <i>p</i> -Acetaminophenyl (1- <i>p</i> -hydroxyphenyl-2-acetylethyl) sulphone.	White crystals, m.p. 152°	$C_{18}H_{19}O_5NS$ (361)	3.89	3.88
III.	$R.CH[C_6H_4.OMe(p)]CH_2CO.Me$ <i>p</i> -Acetaminophenyl (1- <i>p</i> -methoxyphenyl-2-acetylethyl) sulphone	White needles, m.p. 150°	$C_{19}H_{21}O_5NS$ (375)	3.97	3.73
IV.	$R.CH.CH_2CO.Me$   $CH=CHPh$ <i>p</i> -Acetaminophenyl (1-styryl-2-acetylethyl) sulphone.	Brown crystals, m.p. 170° (decomp.)	$C_{20}H_{21}O_4NS$ (371)	3.27	3.77
V	$R.CH[C_6H_4.OH(o)]CH_2COPh$ <i>p</i> -Acetaminophenyl (1- <i>o</i> -hydroxyphenyl-2-benzoylethyl) sulphone.	White prisms, m.p. 133-34°	$C_{25}H_{21}O_5NS$ (423)	3.25	3.30
VI.	$R.CH[C_6H_4.OH(p)]CH_2COPh$ <i>p</i> -Acetaminophenyl (1- <i>p</i> -hydroxyphenyl-2-benzoylethyl) sulphone.	White plates, m.p. 192-93° (decomp.)	$C_{25}H_{21}O_5NS$ (423)	3.70	3.30
VII.	$R.CH[C_6H_4.OMe(p)]CH_2COPh$ <i>p</i> -Acetaminophenyl (1- <i>p</i> -methoxy-2-benzoylethyl) sulphone.	White crystals, m.p. 177-78° (decomp.)	$C_{26}H_{23}O_5NS$ (437)	2.86	3.20
VIII.	$R.CH.CH_2COPh$   $CH=CH.Ph$ <i>p</i> -Acetaminophenyl (1-styryl-2-benzoylethyl) sulphone.	White shining plates, m.p. 164°	$C_{26}H_{23}O_4NS$ (433)	2.86	3.23
IX.	$R.CH[C_6H_4.Br.OH(m)]CH_2CO.Me$ <i>p</i> -Acetaminophenyl (1-2'-hydroxy-5'-bromophenyl-2-acetylethyl) sulphone	Pale yellow crystals, m.p. 174°	$C_{18}H_{18}O_5NSBr$ (440)	2.87	3.18
X.	$R.CH[C_6H_4.OH(o)]CH_2CO.CH=CH.C_6H_4OH$ <i>p</i> -Acetaminophenyl (1- <i>o</i> -hydroxyphenyl-2-β- <i>o</i> -hydroxyphenylacroylethyl) sulphone.	Reddish brown crystals, m.p. 170-71°	$C_{25}H_{23}O_6NS$ (465)	3.29	3.01
XI.	 <i>p</i> -Acetaminophenyl (3,4-dihydrocoumaryl) sulphone.	White plates, m.p. 213-214°	$C_{17}H_{16}O_5NS$ (345)	3.89	4.06

TABLE II  
 $R = NH_2 \cdot C_6H_4 \cdot SO_2 -$

No.	Compounds	General appearance and melting point.	Formula and M. W.	Percentage nitrogen	
				Found.	Calc.
II. a	$R \cdot CH[C_6H_4 \cdot OH(p)]CH_2 \cdot CO \cdot CH_3$ <i>p</i> -Aminophenyl (1- <i>p</i> -hydroxyphenyl-2-acetyl ethyl) sulphone.	White crystals, decomposes at $196-97^\circ$	$C_{16}H_{17}O_4NS$ (319)	4.12	4.39
III. a	$R \cdot CH[C_6H_4 \cdot OMe(p)]CH_2 \cdot CO \cdot CH_3$ <i>p</i> -Aminophenyl (1- <i>p</i> -methoxyphenyl-2-acetyl ethyl) sulphone.	White crystals, m.p. $142-43^\circ$ (decomp.)	$C_{17}H_{19}O_4NS$ (333)	3.91	4.20
VI. a	$R \cdot CH[C_6H_4 \cdot OH(p)]CH_2 \cdot COPh$ <i>p</i> -Aminophenyl (1- <i>p</i> -hydroxyphenyl-2-benzoyl ethyl) sulphone.	Pale yellow needles, m.p. $182-83^\circ$ (decomp.)	$C_{21}H_{19}O_4NS$ (387)	3.41	3.67
VII. a	$R \cdot CH[C_6H_4 \cdot OMe(p)]CH_2 \cdot COPh$ <i>p</i> -Aminophenyl (1- <i>p</i> -methoxyphenyl-2-benzoyl ethyl) sulphone.	White prisms, m.p. $166-67^\circ$	$C_{22}H_{21}O_4NS$ (395)	3.32	3.54
VIII. a	$R \cdot CH \cdot CH_2 \cdot COPh$   $CH=CHPh$ <i>p</i> -Aminophenyl (1-styryl-2-benzoyl ethyl) sulphone.	Pale yellow crystals, m.p. $194-95^\circ$	$C_{23}H_{21}O_3NS$ (391)	3.95	3.58
X. a	$R \cdot CH[C_6H_4 \cdot OH(o)]CH_2 \cdot CO \cdot CH=CH - C_6H_4 \cdot OH(o)$ <i>p</i> -Aminophenyl [(1- <i>o</i> -hydroxyphenyl) 2( $\beta$ - <i>o</i> -hydroxyphenylacryloylethyl)-sulphone.	Dark red crystals, decomposes at $214-215^\circ$	$C_{23}H_{21}O_5NS$ (423)	3.49	3.31

BENGAL IMMUNITY RESEARCH INSTITUTE,  
CALCUTTA.

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## PRAFULLA CHANDRA RAY MEMORIAL LECTURE\*

BY DR. J. C. GHOSH

I am extremely grateful to the Indian Chemical Society for their invitation to deliver the Prafulla Chandra Ray Memorial Lecture this year.

We are meeting today under circumstances which are tragic beyond description. Prafulla Chandra's life was spent in the service of his country—even in serving his favourite science of chemistry, he maintained, he had no other object in life. It was not given unto him to see the dawn of freedom in his country. In some parts of India, that dawn, however, has not ushered in a bright day of hope but threatens to fade into darkness again. Calcutta is the heart of this area. Millions of men have been uprooted from their homes, and the soil which they held as dear as their lives. Many throng the streets of Calcutta—helpless refugees without work; they live in squalor which has to be seen before it can be imagined; many live on doles which just keep the body and soul together. Respectable citizens transformed overnight into homeless wanderers, think of themselves as victims of Fate,—have no will left in them to resist its vagaries. Most of this terribly suffering humanity, however, are cursing the Indian leaders for having agreed to the partition, and are not in a mood to accept with philosophic resignation their present lot.

The thought that comes uppermost to my mind today is "Thy country, Prafulla Chandra, hath need of thee at this crisis in her history". It was at such hours of peril that his abilities shone forth at their best. He never believed in specialisation which kept the spirit bounded and poor. Time and again we have found the scientist laying aside his test tube and leading great movement for the relief of the distressed and preaching new ideas for the moral and material progress of his countrymen, based on self-help. He was never so moved as when he found men driven to sub-human levels of existence due to natural calamities or to forces beyond their control. On such occasions that frail little man could draw as it were, from hidden reserves within himself, superhuman stores of energy, and endow his co-workers with the confidence that where the spirit is willing, the flesh can never be too weak.

I recall vividly even today, how 37 years ago, the student community of Calcutta organised under his leadership relief operations for the sufferers of the Damodar flood of 1913. The embankments on the left side were breached on that occasion at several places and the whole tract now lying to the west of the Calcutta Burdwan chord line was devastated. All the mud houses collapsed, cattle died in thousands and the rice crop was destroyed. The condition of people on the right of the Damodar was much worse: it took days before communication with that area could be restored. I remember well how sons of rich families of Calcutta would come forward as volunteers under the

\* Third Lecture, delivered under the auspices of the Indian Chemical Society on August 2, 1950 at Calcutta.

inspiring influence of Dr. Ray, select, as their group leader, a youngster like Meghnad Saha who knew the ways of life in water logged areas, and carry loads of rice, cloth, salt and medicine to unknown villages wading waist-deep through mud and water. To them such education from the book of life was far more important than what was imparted to them in college classes. Sympathy for the village folk, their useful toil, and homely joys widened the outlook of the city bred youth, while the villager rejoiced in the conviction, that he was remembered when evil days befell him.

Prafulla Chandra was never tired of stating that it is on such strong foundations of understanding, sympathy and devoted service between different groups of men that a true nationhood is built up. It did not require any effort on his part to make himself at home among common people. Living a life of severe asceticism, and spending whatever he had for the benefit of the poor and the oppressed, he naturally gained the unbounded confidence of his countrymen. He was intensely human, and felt a peculiar delight if common people were to mistake him as one of themselves. As a young professor he used to come to College dressed in the cheapest buttoned up coat and trousers that the Chandny Chowk in Calcutta could supply. That dress was familiar to staff and students of Calcutta colleges; but of course not to the passengers at the Sealdah station. And it once happened that he was going to Darjeeling on medical advice to shake off malarial fever and was reclining against his luggages at the platform, waiting for a friend who had gone to the counter to purchase a second class ticket. A chaprasi of a European passenger accosted him by saying "Hallo, you are also waiting for your master as I am doing". "Where does your master stay in Darjeeling" and so on. Prafulla Chandra was answering these questions as best as he could without revealing his identity, when somewhat to the discomfiture of the chaprasi, the European passenger came and happening to recognise him, shook him by the hands.

They say that truth lived is a thousand time more potent than truth spoken. Words acquire a new meaning depending upon the person who speaks them. Likewise, thoughts acquire a new significance depending upon the person who expresses them. A word of hope and sympathy from Prafulla Chandra put more strength and courage in suffering humanity than all the good wishes of bureaucrats and intellectuals. An appeal from him for help would evoke response from the remotest corner of the country. Even a stony heart softens by touch with another which melts at sight of distress. And so when the great flood of 1922 overwhelmed North Bengal, and created unprecedented havoc, people rushed to him and acclaimed him as the leader for organising relief. How well he did this work has been thus narrated by a special representative of the Manchester Guardian :—

"There was a heavy rainfall from the 25th to 27th September, and the water rose to an unprecedented height. Throughout 700 sq. miles of a thickly populated countryside, more than half the houses collapsed, 12,000 heads of cattle perished, all fodder was ruined and the main crop was utterly destroyed. Government seemed to have no conception of the gravity of the situation. They were slow to move, the action taken was inadequate and what they gave was given ungraciously..

"In these circumstances a professor of chemistry, Sir P. C. Ray, stepped forward and called upon his countrymen to make good the Government's omissions. His call was answered with enthusiasm. The public of Bengal in one month contributed three lakhs of rupees; rich women giving their silks and ornaments, and the poor giving their spare garments. Hundreds of youngmen volunteered to go down and carry out the distribution of relief to the villagers, a task which involved a considerable amount of hard work and bodily discomfort in a malarious country.

"What greatly aggravated the public's dissatisfaction with Government's attitude was the fact that the disaster is generally attributed to the faulty design of the railways which is believed to make very inadequate provision for the passage of flood water. There is much evidence to support this view, but it was only after a lapse of a month and a half that Government promised an enquiry into the question.

"The enthusiasm of the response to Sir P. C. Ray's appeal was due partly to the Bengali's natural desire to score off the foreign Government, partly to genuine public sympathy with the sufferers, and very largely to Sir P. C. Ray's remarkable personality and position. Sir P. C. Ray is a scientist of world-wide repute. I do not think he can be said to be an orthodox Non-Co-operator, but he is a very strong Nationalist, and a very strong critic of Government. He is also a real organiser and a real teacher. I heard a European saying, 'If Mr. Gandhi had only been able to create two more Sir P. C. Rays he would have succeeded in getting Swaraj within this year'. A Bengali student told me, 'If any Government officer or any of the non-co-operating politicians had called for subscriptions the public would not have given even three farthings. But when Sir P. C. Ray calls everyone knows that the money will be spent and well spent, and not wasted.' I had the good fortune to see Sir P. C. Ray in Calcutta at his College of Science and I think I can understand why his fellow-countrymen feel so much confidence in him. One day he was gloating over vast and disorderly-looking stores of clothes, old and new, brought by Bengali sympathisers to his laboratories. The volunteers were busy under his eyes, bringing order out of disorder, and arranging for the despatch of the clothes to the scene of the relief operations. The next day I caught a glimpse of him assisting two young students to carry out some experiment in chemistry, and it seemed to me there was affection between the teacher and the taught. When I heard him talking about the Government I felt that I would sooner serve under him than be criticised by him. He is too warm-blooded and energetic a man to make a perfectly fair critic. But any man who feels aggrieved by his criticism has at least the satisfaction of knowing that unlike so many critics, Sir P. C. Ray would never shirk taking on the job himself if the chances were offered him, and that if he did take on the job he would be likely to put it through about as well and perhaps a little better than everybody else.

"My enquiries on the spot made it quite clear that Government have lost immensely in prestige over the whole affair, and that Non-Co-operation has won what Government have lost, thanks to the fine work of Sir P. C. Ray's volunteers."

Prafulla Chandra was like a gem with many facets radiating light in many directions. I have naturally taken as my first theme that facet which gives us a vision of democratic life in the Union of India, where each member of the Society palpitates

with true humanitarian feeling, when another elsewhere is adversely affected ; where the diverse elements in our cultural and economic life are cemented together, as in a mosaic, by forces of love and good will.

To Fellows of the Indian Chemical Society, Prafulla Chandra's work as a Scientist is generally known. It is time, however, that some of his old students prepare a complete review of his researches, and interpret some of his experimental results in the light of newer ideas. As a boy he was passionately fond of studies in history and literature ; while at Albert School, he came under the influence of the Rector, Krishna Behary Sen who was also the editor of the Indian Mirror which the young student read with eagerness every morning before the classes began. He resolved that when he grew up, he would wield as facile a pen as Krishna Behary. Being of studious habits, he read whatever books were there in his father's library. Even Johnson's Dictionary in two quarto volumes caught his fancy, and he committed to memory hundreds of apt quotations from classical authors. One such quotation he would often repeat in later life to his students "Ignorance is the curse of God, Knowledge the wing wherewith we fly to Heaven." In the Tatwa Bodhini Patrika, the organ of the Brahmo Samaj, he read with the greatest appreciation, the writings and sermons of Debendranath Tagore, Keshab Chandra Sen, Rajnarain Basu ; and from these it was but another step to come to Raja Ram Mohan Ray. A window in his mind was opened, as it were, by the famous letter of Ram Mohan Ray to Lord Amherst in 1822 advocating "the promotion of a more liberal and enlightened system of instruction including mathematics, natural philosophy, chemistry, anatomy and other useful sciences, which may be accomplished by employing a few gentlemen of talent and learning, educated in Europe and providing a College furnished with necessary books, instruments and other apparatus". Even half a century later, this hope of Ram Mohan that modern science should dominate the education of Indian youth had remained an empty dream. Franklin's biography he read over and over again, and there he was struck by the observation, so allied to that of Ram Mohan that the most certain method of human betterment was improvement in natural knowledge. The die was cast. Shakespeare and Madhusudan, Gibbon and Rajendra Lal Mitra must take back seats in the garden of his mind. He would devote himself to the study of modern sciences.

Prafulla Chandra was born with a silver spoon in his mouth. But even before he completed his school education the family estates dwindled into insignificance due to the debts incurred by his father ; there was therefore no hope that he could be given any help from home for scientific studies in Europe. To this handicap was added the more serious one of a fragile constitution. At the age of 13 his health was almost wrecked by an obstinate attack of dysentery, which impaired his digestive organs and arrested his natural growth during adolescence. He had to discontinue his studies in school for more than 2½ years and to submit himself, ever after, to a strict dietary discipline. But these handicaps only spurred young Prafulla to greater efforts. While reading for his degree with physics and chemistry as his optional subjects, he was secretly preparing for the Gilchrist scholarship examination which required a fair acquaintance with Latin, Sanskrit and French. It was an All-India competition and his success in 1882 gave him the cherished opportunity for proceeding to Great Britain

for higher studies. He entered the University of Edinburgh in October, 1882, and his subjects of study were chemistry, physics, botany and zoology. In chemistry he came under Crum Brown, whom he learnt to esteem, and with fellow students like Hugh Marshall Alexander Smith, James Walker, the atmosphere was such that he became passionately fond of chemistry. His studies for the B.Sc. degree were interrupted for a time when he competed for a prize on the best essay on "India, before and after the mutiny". In this "he indulged in many bitter diatribes against the British Rule" and the essay was judged among those *Proxime accesserunt*. It did, however, one good thing—Ray discovered that he had the faculty of writing with facility, a faculty which he used with great power in later life.

The essay written, he worked hard in his favourite subject of chemistry and obtained the D.Sc. degree in 1888 on the basis of a thesis in inorganic chemistry. He was honoured in due course by the award of a special scholarship by the Gilchrist Foundation and of the Hope Prize Scholarship, and also by his election to the position of Vice-President of the Edinburgh University Chemical Society. The simple life and the cheap living of those days in a Scottish University made an abiding impression on him. Students left to fend for themselves at an early age and protected by poverty from vicious amusements—lived in an atmosphere of high endeavour, in which University education was of real value as a preparation for life.

He now tried to join the Indian Educational Service; but high honours at the University, strong testimonials from professors of repute and powerful recommendations from well-wishers like Sir W.M. Muir and Sir Charles Bernard were of no avail at the India Office in London.

He returned to Calcutta in 1888 and, after a year of waiting, obtained the post of an assistant professor at the Presidency College, Calcutta on Rs. 250 a month. Persons with inferior qualifications were holding high appointments as professors in the Indian Educational Service, and he naturally felt the injustice that had been done to him. But he was determined to make the best use of his opportunities. In Europe the reputation of a professor depends more on his capacity for extending the bounds of knowledge rather than that for actual teaching. But in India this tradition was sadly lacking. From the very beginning of his career Dr. Ray felt it to be his mission in life to bring this tradition of Europe into the atmosphere of Indian Universities and to create an enthusiasm for research in his young students.

His training in Edinburgh was primarily in the field of Inorganic Chemistry and his researches in the early days of professorship were mostly confined to this branch of knowledge. His contributions till 1896, when he discovered mercurous nitrite, were mostly of a routine type which gave indication of high skill in preparation and analysis. But from 1896 till 1920, he devoted himself to the study of nitrites. Of this work extending over a quarter of a century Prof. Armstrong remarked as follows:

The way in which you have gradually made yourself "master of nitrites" is very interesting and the fact that you have established that, as a class, they are far from the unstable bodies, chemists had supposed, is an important contribution to our knowledge.

He extended his researches later to the field of organic sulphur and organo-metallic compounds. Many of his colleagues did not like the foul smell that came out of his laboratory, but he himself seemed to be oblivious of it. With the discovery of Vitamin B<sub>1</sub> as a sulphur compound, the indifference to the handling of sulphur compounds has disappeared, but it was not so when Dr Ray worked in this field. He was not so much interested in the synthesis of these compounds as in the nature of the chemical reactions which resulted in their formation. Long chain sulphur compounds obtained by the reaction of dithioethylene glycol with ethylene bromide, excited him immensely, but modern theories of polymer formation were not there to guide him in these researches and carry forward the investigations to their logical conclusions.

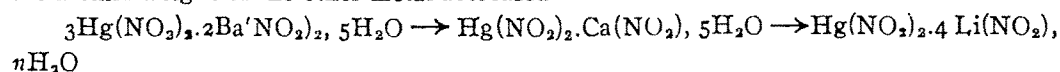
I would, today, from more than two hundred papers bring to your notice a few that, in my opinion, may give you an idea of the scope and value of his work.

*Mercurous nitrite* (J. Asiatic Soc., 1896), obtained as yellow thin crystals when dilute nitric acid containing 13 to 14% of N<sub>2</sub>O<sub>5</sub> reacts with mercury in the cold. The *Nature* remarked that the Journal of the Asiatic Society can scarcely be said to have a place in Chemical Libraries, but this number contained a paper by Prof. Ray, on mercurous nitrite which is worthy of note.

*Mercuric hyponitrite*.—A neat method of preparation is by interaction of mercuric nitrite with potassium cyanide whereby cyanide is oxidised to cyanate and nitrite reduced to hyponitrite (J. C. S., 1897).

*Preparation in the pure state of the nitrites of alkaline earths* (J. C. S., 1905), magnesium nitrite being the least stable and forming a link between the nitrites of zinc and cadmium and those of calcium, strontium and barium.

*Preparation of the double nitrites of mercury (ic) with alkali and alkaline earths.* (J. C. S., 1910).—The combining power of mercuric nitrite was found to increase as the atomic weight of the other metal decreased



*Nitrites of the mercuri-alkyl or aryl ammonium series* (J. C. S., 1912).—The molar conductivity of mono-amine salts is similar to alkali metal nitrites, while ethylene-diamine salts behave as alkaline earths nitrites. The complexes may be represented as  $[\text{R NH}_2 \cdot \text{HgNO}_2] \text{NO}_2$  and  $[\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot \text{Hg}] (\text{NO}_2)_2$ .

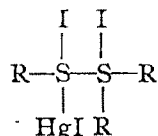
*Methyl ammonium nitrite, nitrites of the alkyl ammonium bases: Tetramethyl ammonium hyponitrite* (J. C. S., 1911).—Unlike mercuric nitrite which yields complex salts with alkyl or aryl amines, double decomposition of silver nitrite with alkyl amine hydrochlorides in cold aqueous solution gave nitrites of the alkyl ammonium series. Prof. Dey who was associated with Dr. Ray in these researches has given an illuminating account of this work from first hand knowledge in the last year's memorial lecture.

*Decomposition and sublimation of ammonium nitrite: Vapour density of ammonium nitrite* (J. C. S., 1909, 1912).—In noticing these papers, *Nature* (Aug. 13, 1912) remarked that Prof. Ray has added to his success in preparing ammonium nitrite in a tangible form, a further accomplishment in determining the vapour density of this very fugitive compound. This paper on vapour density in which Dr. N. R. Dhar was his collaborator was read by Prof. Ray in a crowded meeting of the London Chemical Society at the end of which Sir William Ramsay and Dr. Veley paid a warm tribute to Dr. Ray and his pupils for their valuable researches on ammonium and amine nitrites.

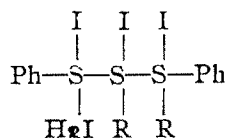
*Velocity of decomposition and the dissociation constant of nitrous acid* (J. C. S., 1917).—This paper is of peculiar interest to me (J. C. Ghosh) as I had the privilege of collaborating with Dr. Ray in this research. It was shown that a solution of nitrous acid can be obtained at 0°C by double decomposition, that it can be concentrated by freezing out the solvent water, that it decomposes with a monomolecular velocity constant, that its dissociation constant as a weak acid can be approximately estimated. It was also noticed, contrary to expectation, that nitrous acid as such reacted very slowly with urea—an observation which was utilised by Wiener in postulating a new constitution of urea.

#### *Mercaptans and Mercaptides*

Dr. Ray's abiding interest in mercury nitrites led him to study reactions of mercuric nitrite with mercaptans (J. C. S., 1916, 131, 603). The resulting nitromercaptides of the formulae  $\text{RSHgNO}_2$  and  $\text{RSHg}(\text{NO}_2)_2$  gave complex sulphonium compounds of the type  $\text{R}_2\text{S}_2\cdot\text{HgI}_2\cdot\text{R}\cdot\text{I}$  which were represented by the formula



Crystals of the compound  $\text{I}\cdot\text{Hg}\cdot\text{S}\cdot\text{S}\cdot\text{Hg}\cdot\text{I}$  exhibit remarkable phototropism. Potential mercaptans behaved similarly or formed complexes. For example, with 2:5-dithiol-1:3:4-thiodiazole gave a trinuclear condensation product  $(\text{C}_2\text{N}_2\text{S}_3)_x\text{Hg}_2\text{O}$ , where  $x=2, 3, 4$  or 6. These furnished on interaction with alkyl iodides long-chain sulphonium compounds (J. C. S., 1919, 261, 541). Phenylmercaptan gave a mercaptide of the formula  $\text{Ph}_2\text{S}_3\text{Hg}$ , which yielded the sulphonium compound



$\alpha$ -Naphthyl mercaptan behaved similarly (J. C. S., 1919, 1148).

The study of these complex sulphur compounds led him to investigate the formation and behaviour of some organic sulphides and mercaptans, actual and potential (J. C. S., 1922, 323). It was shown that chloropicrin could be conveniently used as a reagent for the diagnosis of real and potential mercaptans. The latter invariably parted with some sulphur in the free condition when the reagent was added, but the former did not. Thiocarbamide and thioacetamide behaved like real mercaptans towards  $\text{HgCl}_2$ ,  $\text{PtCl}_4$  and  $\text{CuCl}_2$  (J. C. S., 1919, 871).

Interaction of ethylenedibromide and alcoholic KSH gave the compound  $\text{HS}(\text{C}_2\text{H}_4\text{S})_2\cdot\text{C}_2\text{H}_4\text{SH}$  and the corresponding tetrasulphide  $(\text{C}_2\text{H}_4)_3\text{S}_4$  along with a trisulphide of the formula  $(\text{C}_2\text{H}_4)_3\text{S}_3$  and more complex polysulphides (J. C. S., 1920, 1090).

*The oxidation of triethylene tri- and tetra-sulphides.*—Triethylene-trisulphone was obtained with permanganate, and with nitric acid, a disulphone. Benzylidene-diethylene

tetrasulphide and benzylidene-diethylene trisulphide were obtained by the interaction of dithioglycol and benzylidene chloride, byproducts being diethylene disulphide and diethylene tetrasulphide (*J. C. S.*, 1923, 2174; 1925, 1141).

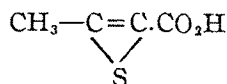
Trimethelene dibromide gave, besides the expected mercaptan, the corresponding disulphide (*J. I. C. S.*, 1919, 865).

Dithioethylene glycol and ethylene bromide furnished a very interesting series of long-chain compounds of the type  $\text{BrC}_2\text{H}_4(\text{SC}_2\text{H}_4)_n\text{Br}$  (*J. I. C. S.*, 1926, 75). In this way macromolecular sulphur compounds were obtained.

Studies on the tautomeric changes of chain compounds showed that thiocarbamide passes on to the thiol configuration in presence of monochloroacetic acid (*J. C. S.*, 1914, 2159; 1916, 698). Similar tautomeric changes were induced in thiocarbamide, thioacetamide and thiobenzamide by mercuric nitrate, mercuric chloride, cupric chloride, platinic chloride and iodine.

Some mercaptans of the purine group were synthesised for the first time (*J. C. S.*, 1923, 1957) and condensed heterocyclic systems were derived by the action of organic halides on 2:5-dithiol-1:3:4-thiodiazole (*J. C. S.*, 1919, 1308). Complex products were also obtained from 2-thiol-5-thiol 4-phenyl-4:5-dihydro-1:3:4-thiodiazole and 2:5-dithiol-1:3:4-thiodiazole and organic halides (*J. I. C. S.*, 1926, 23).

Thioacetamide and monochloroacetic acid in acetone gave the interesting compound  $\alpha$ : $\beta$ -thiocrotonic acid (*J. C. S.*, 1917, 507)



Ethyl thioacetoacetate and ethyl thioacetone dicarboxylate were obtained from ethyl acetoacetate and acetone dicarboxylate by their interaction with  $\text{H}_2\text{S}$  and  $\text{HCl}$  in alcohol. S-Alkyl derivatives of ethyl thioacetoacetate  $\text{CH}_3-\text{C}(\text{SR})=\text{CH}.\text{CO}_2\text{Et}$  was obtained from ethyl thioacetoacetate and alkyl iodide (*J. C. S.*, 1933, 75). Acid hydrolysis of these compounds yielded mercaptans and acetone whereas alcoholic potash furnished alkylated mercaptocrotonic acids.

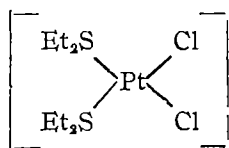
Oxidation of triethylene tetrasulphide with nitric acid was found to produce ethylene disulphonic acid, but potassium permanganate gave the expected tetrasulphone which combined with metallic sulphates to form a new and interesting series of double salts (*J. C. S.*, 1924, 207). Hydrolysis of allyl thiocarbamide resulted in two isomeric allyl amines, b. p.  $53-54^\circ$  ( $\text{HCl}$ ) and  $57-58^\circ$  ( $\text{H}_2\text{SO}_4$ ) (*J. Asiatic Soc. Bengal*, 1912, 8, 371).

The most important contribution of Sir P. C. Ray on organo-metallic complexes are those which led him to postulate varying valencies for platinum, gold and iridium. These postulates have been proved by a series of careful experiments which involved the interaction of platinic, gold and iridium chlorides with organic sulphides and mercaptans. For example, with dithioethylene glycol platinic chloride forms the complex of the formula  $\text{Pt}(\text{SC}_2\text{H}_4\text{SH})_x$ , where  $x=3, 4, 5, 6$  or  $8$ , the platinum in these compounds functioning as ter-, quadri-, quinque-, hexa- or octa-valent according to experimental conditions.

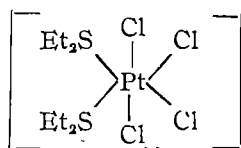
Diethyl sulphide similarly produced a series of compounds, viz., (a)  $\text{PtCl}.\text{Et}_2\text{S}$ ; (b)  $\text{PtCl}_2.2\text{Et}_2\text{S}$ ; (c)  $\text{PtCl}_3.2\text{Et}_2\text{S}$ ; (d)  $\text{PtCl}_4.2\text{Et}_2\text{S}$ ; and (e)  $\text{PtCl}_5.2\text{Et}_2\text{S}, 2\text{H}_2\text{O}$ . Of



these, the compound (b) has been isolated in six isomeric forms and constitution of three of them has been accounted for in the following way : (1) Blomstrand's *cis*-compounds, (2) Blomstrand's *trans*-compounds and (3)  $[\text{Pt}(\text{Et}_2\text{S})_4]\text{PtCl}_4$ . Compound (c) is regarded as a molecular compound of (b) and (d). This has been proved by separation of the two constituent molecules on crystallisation from alcohol and confirmed by the action of ammonia. Compound (e) shows a higher co-ordination value than six. Similar compounds have also been obtained from benzyl sulphide. Compound (b) and compound (d) are represented by the following co-ordination formulae :



(b)



(d)

The constitution of these complexes were also studied by interaction with organic bases and determining their ionisabilities.

With mercaptanic radicals gold, like platinum, forms compounds in which it behaves as a bi-, ter-, quadri- or quinque-valent atom (*J. Indian Chem. Soc.*, 1924, 1, 63 ; 1928, 5, 527 ; 1930, 7, 67). An example of bivalent gold is furnished by the crystalline compound  $2\text{AuCl}_2.\text{Et}_2\text{S}_2$ . With dithioethylene glycol, the compound  $2\text{AuCl}(\text{C}_2\text{H}_4\text{S}_2)_2$  is obtained. This is regarded as a compound containing bi- and tervalent or quadrivalent gold. An example of quinquevalent gold is furnished by the compound,  $(\text{C}_2\text{H}_4\text{S}_2)_5\text{Au}_3$ . That medium has a profound influence on the valency of gold is proved by the fact that, in acetone, dithioethylene glycol and gold chloride form the above compound, but a different compound, viz.,  $\text{Au}_3\text{Cl}(\text{C}_2\text{H}_4\text{S}_2)_4$ , in which gold is tervalent is obtained in ethereal solution. A series of compounds where gold assumed different valency conditions was also obtained by treating gold with some other organic sulphides, particularly, 1:1-dithian

From iridium chloride the following compounds were obtained (*J. Chem. Soc.*, 1923, 276 ; 1932, 251) :  $\text{IrCl}_3.3\text{Me}_2\text{S}$ ,  $\text{IrCl}_3.2\text{Me}_2\text{S}$ ,  $\text{Ir}_2\text{Cl}_6.4\text{Me}_2\text{S}$ ,  $\text{IrCl}_3.3\text{Et}_2\text{S}$  (*cis*- and *trans*-isomer). Similar compounds were obtained from dibenzyl sulphide.

Other metallic complexes obtained are  $\text{AgNO}_3.\text{R}_2\text{S}$ ,  $\text{AgNO}_3.\text{R}_2\text{S}_2$ ,  $\text{SbCl}_3.\text{R}_2\text{S}$  (*J. Indian Chem. Soc.*, 1931, 8, 711, 689).

His last contribution related to fluorination of organic compounds (*J. Chem. Soc.*, 1935, 93 ; 1936, 427). This was achieved by double decomposition of anhydrous thallus fluoride with reactive organic bromo compounds. Ethyl and methyl fluoromates, fluoroacetone, fluoroacetal etc. were thus obtained.

In recognition of these researches, Dr. Ray was elected in 1934, an Honorary Fellow of the Chemical Society of London. Sir Gowland Hopkins and Professor C. Matignon were the two other recipients of this honour on this occasion. This appreciation of his services by his fellow chemists of the Commonwealth touched him deeply.

Side by side with the pursuit of these researches, which he was carrying out in the laboratory, he was also indulging in his favourite hobby—researches into the History of Chemistry. But it was not long before he fell a victim to insomnia and for more than half a century he was unable to do any literary work at night, as every such effort kept

him awake for several nights in succession. "Early to bed and early to rise" became his motto and he spent religiously a couple of hours in the morning for serious study. Encouraged by the French Savant Berthelot, he instituted a vigorous search for Sanskrit manuscripts bearing upon Chemistry and Alchemy. The results of these studies was embodied in the "History of Hindu Chemistry" of which the first volume was published in 1902. This monumental labour of love was welcomed with high encomium both in India and outside as adding a very interesting chapter to the history of sciences and and of the human spirit. The Vice-Chancellor of the University of Durham in conferring on Dr. Ray the honorary degree of D.Sc. referred to this monumental work "of which both the scientific and linguistic attainments are equally remarkable, and of which, if of any book, we may pronounce that it is definitive." In this self-imposed task, Dr. Ray was guided by the hope that a rediscovery of the glories of the past might bring to his countrymen; confidence in a bright future.

To him, the foundation of the Indian Chemical Society was the realisation of a long cherished dream. It took tangible shape in 1920 when as a result of his fourth visit to England he realised that Indian contributions to the knowledge of chemistry were so rapidly expanding that the Journal of the Chemical Society, London, might find it difficult to arrange for their publication. It happened that Bhatnagar, Mukherjee and Ghosh were then working in the laboratories of Professor Donnan in London. They were fortunate in that they had each a small research room for their use; and Bhatnagar being a vegetarian, they often prepared simple lunch in Indian fashion in the laboratories. The "Chelas" gave a standing invitation to the "Guru" to partake of this simple midday fare, which he often did. In one of these luncheon meetings, the trio pledged themselves to the proposition that on return to India, they would spare no efforts to bring into being the Indian Chemical Society with Dr. Ray as the first President. Mukherjee willingly offered to take up the onerous task of the first Secretary of the Society. The Society was founded in 1924 with a journal of its own; and in reply to congratulations from the President and Council of the Chemical Society, London, Dr. Ray wrote as follows:—

"The J. C. S. has hitherto been the only organ of chemists throughout the British Empire, and the Publication Committee have been hard put to it to find space for the ever-increasing number of communications and have often been under the necessity of appealing to authors of papers to abridge them as far as possible. This will explain the necessity of founding the Indian Chemical Society, with an organ of its own.

More than 40 years ago, while a student at Edinburgh, I almost dreamt a dream that, God willing, a time would come when modern India would also be in a position to contribute her quota to the world's stock of scientific knowledge, and it has been my good fortune to see my dream materialise. I have shown in my History of Hindu Chemistry that this branch of science was zealously pursued in ancient India and I have now the satisfaction of finding chairs of Chemistry in most of the Universities of India filled by my own pupils, who have also been regular contributors to the J. C. S. .... I can scarcely suppress the feelings which arise in me as I am penning these lines. Thanking you once more for your good wishes,

Yours etc.,  
(Sd). P. C. RAY.

The last two lines of the letter quoted above could have been only written by a great teacher who would seek victory every where but would consider that day the proudest in his life, when his own student surpasses him in attainments—

सर्व्वत्र जयन्निष्ठे पुनार् शिष्यात् पराजयम् ।

In his autobiography he writes of his lecture work as follows :—

“Throughout my twenty-seven years career at the Presidency College, I made it a point to lecture mainly to the junior classes. Boys coming fresh from High Schools are very teachable as they represent so much clay in the potters hand to be moulded into the desirable shape. My lectures were never based upon any particular text-books. A good portion of the session—July, August and September—was taken up in finishing the three elements, namely oxygen, hydrogen and nitrogen, as also their compounds. I took good care to give my pupils an historical insight by weaving into my lectures—stories of the discovery of oxygen—the contributions of Priestley, Lavoisier, and Scheele and their rival claims. Under the oxides of nitrogen, again, the atomic theory, specially the law of definite and multiple proportions, was given prominence and Dalton was brought on the stage so to speak and a sort of living personal contact was sought to be established between ‘the makers of modern Chemistry’ and my pupils. In short, I took good care to have the groundwork on a solid foundation.”

He believed “that the business of the university was not the transformation of undergraduates into fountains of knowledge. Its business is the difficult task of teaching students how facts are converted into truth. A mind receptive to novelty, capable of wisdom, inclined to moderation—these are the excellences at which it aims. The university has failed when its students are not aroused to passionate discussion amongst themselves or awakened to the study of great books ” In his class room, topics were often discussed which had sometimes nothing to do with chemistry. Thus speaking of glass as impervious to water and non-conductor of heat, he would suggest that water inside such a glass tumbler handed over by a sweeper cannot be polluted and would proceed to drink that water and invite the students to do so ; or that bones of cattle when burnt become inorganic calcium phosphate and that such burnt bits of bones may be chewed by Hindus. Speaking of Cavendish he would say how the great scientist felt extremely nervous in the presence of ladies, and would add that he did not know how he would himself fare in a similar situation. He would also lament that sons of the well-to-do in India never indulge in hobbies which extend the bounds of knowledge. He would describe how the self-taught Davy isolated the alkali elements and proved the elementary nature of chlorine. He would then narrate the history of the Royal Institution—the epoch-making discoveries of the Professors there culminating in the work of Dewar who liquified hydrogen when he was working there on deputation from India as a guest professor. Or he would describe how Berzelius in a small private laboratory made epoch-making contributions with the help of one laboratory assistant who was also the maid of the house, and how, after reading Davy’s memoir he exclaimed “Hearest thou Anna, thou shalt not in future call chlorine, oxy muriatic acid”. Discussing how Cannizzaro resuscitated the famous hypothesis of Avogadro, he would describe how Cannizzaro once shut up his laboratory, and shouldered the musket, exclaiming that “science can wait, but fight for freedom cannot”.

There was rarely a student in the B. Sc. Honours classes in chemistry of the Presidency College who did not know Dr. Ray personally and had not confided in him his hopes and aspirations and even his personal joys and sorrows. The result was that most of the bright and adventurous students after taking their Honours degree, would prepare a thesis under his guidance in lieu of a part of the examination for the M.Sc. degree. This helped the rapid expansion of a school of chemistry, seeds of which were sown in the first decade when he started taking research students as collaborators.

He retired from the Presidency College in 1916, to join the University College of Science as the Palit Professor of Chemistry on the invitation of the maker of the modern University of Calcutta - Sir Asutosh Mookerjee. The farewell address quoted below moved him to tears:-

"Your place in the college, Sir, we are afraid, can never be filled. Men will come and men will go but where else can we possibly expect to find again that sweetness of disposition, that vigour of simplicity, that unwearied spirit of service, that broadbased culture, that wisdom in deliberation and debate which for the space of thirty years or more endeared you so much to your pupils?

Yours was, Sir, indeed no small achievement. Your way of life, with its distinct Indian traits, recalled us to the sweet and simple and manly days of Indian attainment. You have been to us all through a guide, philosopher and friend. Easy of access, ever-pleasant, ever-willing to help the poor and needy student with your counsel and your purse, living a life of study, celibate simplicity, with genuine patriotism, not loud but deep, you have been to us an ancient Guru reborn, a light and an inspiration from the treasure-house of old Indian spirituality.

When the history of India's intellectual attainment in the modern era comes to be written, your name will be mentioned in the very vanguard of progress as the maker of modern chemistry in India. The credit and the glory of being the pioneer in the field of chemical research and of giving the impetus to scientific curiosity in this country is yours. Your 'History of Hindu Chemistry' has opened a new chapter of Indian attainment and built a bridge over the abyss of the past whereon our researchers may shake hands with the spirits of a Nagarjuna and a Charaka.

And you have effected more. The theoretical study of chemistry has impelled you to its application to the natural resources of the country and the Bengal Chemical and Pharmaceutical Works is a living testimony to what un-aided Indian Science and business organisation can accomplish.

In the evening of your life, Sir, when men seek for rest and repose, you have preferred to remain in harness, to make the torch of Science you lighted a generation ago, burn steady and clear! May the College of Science and the cause of chemical research profit long by your untiring zeal! May many more and yet many more groups of eager investigators be sped on this path with your blessing!"

In his reply he expressed the hope that the fire which had been kindled in the hearts of young men to extend the bounds of knowledge would be kept burning on from generation to generation of our students till it illuminated the whole of our motherland. If any one were to ask him what treasures he had piled up at the end of his career,

he would, like Cornelia of old, point to the bright young men who had joined him in the quest of the unknown in the frontiers of Science.

The hopes of Sir Asutosh that Government would come forward with generous contributions to supplement the princely endowments of Sir Tarak Nath Palit and Sir Rash Behary Ghosh, for building up the College of Science, were not fulfilled. The University was only permitted to spend Rs. 12,000 a year from the Imperial grant for the upkeep of the laboratories. Men in high places in Indian public life, were not wanting, who compared this paltry help with the generous assistance from public funds given to the Indian Institute of Science at Bangalore and the Royal Institute of Science at Bombay and drew the conclusion that the prejudice against Science College, Calcutta, arose from the condition of the Trust deeds that none but Indians should hold the Chairs. Dr Ray decided that the salary payable to him as Professor should be spent for the development of the Chemistry Department of the College. In 1936 he retired from active service and was appointed Emeritus Professor of Chemistry in the University of Calcutta. Of him, as a teacher of youth, as a Guru inspiring his disciples with high ideals and the spirit of conquest in the domain of knowledge, Rabindranath wrote as follows:-

“ It is stated in the Upanishads that the One said, ‘I shall be many’. The beginning of creation is a move towards self-immolation. Acharya Prafulla Chandra has become many in his students and has made his heart alive in the hearts of many. And that could not have been at all possible had he not unreservedly made a gift of himself. This power of creation having its inception in self-sacrifice is a divine power. The glory of this power in the Acharya will never be worn out by decrepitude. It will extend further in time through the ever-growing intelligence of youthful hearts; by steady perseverance they will win new treasures of knowledge.”

Great as he has been as a teacher, he has also proved a most successful man of action. He has been responsible for establishing many industrial enterprises, of which the creation of the Bengal Chemical and Pharmaceutical Works is the most remarkable. When, as a young D.Sc. of Edinburgh, he was trying to secure an appointment in the Education Department, the Director of Public Instruction told him once that if he was such a clever chemist why did he not start industries. The young professor felt that the cheap and innumerable raw materials of Bengal could be converted into costly finished products with the aid of the scientific knowledge that he commanded.

Unaided, and with a capital of a few hundred rupees saved from his small salary, he began the preparation of pharmaceuticals at his own home. His duties at college were exacting. His research work in the laboratory continued every day from 10-30 A.M. to 5 P.M., his health was much below normal, but the will to achieve success as an industrialist was unconquerable.

In a few years the house at 91, Upper Circular Road, except for the bed-room which he occupied, had the appearance of a factory. His pharmaceutical preparations soon secured well-merited recognition and the business rapidly expanded. In 1902 the Bengal Chemical and Pharmaceutical Works were converted into a limited concern with a capital of 2 lakhs of rupees, and Sir Prafulla made over his share in the concern to a trust created for conducting a High School and other beneficent activities in his

native district of Khulna. Today, the Bengal Chemical and Pharmaceutical Works is the biggest concern of its kind in India and with branch factories at Bombay and Kanpur, manufactures and sells goods worth one and half a crore of rupees every year.

Dr. Ray was a close associate of Sir M. Visveswaraya in the campaign-Industrialise or perish. Ever since his retirement from Government service he had given freely of his money, his time and his advice to all who were prepared to take reasonable risk in developing new industries and in his public speeches, he would give high praise to pioneers who from small beginnings had built up industries which gave gainful occupation to our countrymen and reduced the dependence of India on foreign countries for her essential needs.

A man of wide culture, interested in almost all activities of human life, he came to occupy in his later years, a unique position in the public life of the country. He travelled far and wide all over India; there was no nook and corner of his home province of Bengal with which he was not familiar. As he himself expressed it, sooner or later he found himself "the property of anybody and everybody, and was called upon by various educational institutions, by conferences, by the periodical papers and by all those interested in the development of industrial and political life of India to address his countrymen on subjects which so closely affected their national welfare and and prosperity". He was a man of indomitable will. A life-long sufferer from dysentery and insomnia, he took these maladies very lightly. He would even tell us "if you wished to live a long and useful life, you should nurse an incurable disease," and he would give examples of scores of people who had done so. He regretted nothing more than time wasted. And so, we find, that in the evening of his life when others would have taken well-earned rest, he was moving about from place to place, day in and day out, exhorting his countrymen to be self-reliant, not to resign themselves to fate, but build up their future on their own efforts, reminding them that the key to the success of the western nations was their belief that they can make their own future. He appealed to the middle classes of Bengal to place enterprise ahead of security, to take to pursuits involving manual work and to banish from their minds the craving for salaried jobs. The story of such a life, as Professor Armstrong wrote, is not only fascinating; it has an altogether special value as a presentation of a complex mentality unique in character, range of ability and experience—a life over-full of action, of unusually varied occupations and interests, of the highest endeavour, ever pulsating with vitality and intellectual force.

One often wonders—what is there beyond death? But Prafulla Chandra will not die. He will ever live in the hearts of his countrymen!

JAI HIND!

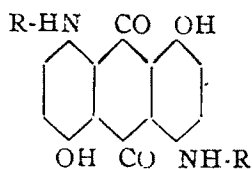
## ARYLAMINO DERIVATIVES OF ALIZARIN

R. P. GONSALVES, A. N. KOTHARE AND V. V. NADKARNY

A few 4-arylamino derivatives of alizarin have been synthesised and their dyeing properties investigated.

It is well known that nitro groups can be replaced by  $\text{NH}_2$  by the action of ammonia (Puzibram, D.R.P., 6,256), or by  $\text{NH-R}$  and  $\text{N} \begin{smallmatrix} \text{R}_1 \\ \text{R}_2 \end{smallmatrix}$  by the action of primary and secondary amines (Baeyer, D.R.P., 139,581; 144,634; 136,777-8) or by primary aromatic amines (*Ber.*, 1913, **46**, 2702; Baeyer, D.R.P., 125,578; 126,803; 148,767; 150,332). The action of primary and secondary aliphatic as well as primary aromatic amines on nitroanthraquinones has been investigated. Secondary aromatic amines do not react with nitroanthraquinones; the tertiary amines, on the other hand, reduce the nitro groups to amino groups (Baeyer, D.R.P., 147,851). Further, it has been observed that the nitro group in  $\alpha$ -position reacts with the arylamines, while that in the  $\beta$ -position is not sufficiently reactive (Wedekind and Co., D.R.P., 235, 776; 244,372; 245,014; 247,245). Kauffler (*Ber.*, 1903, **36**, 65) for instance, states that 2-nitroanthraquinone is unaffected by boiling with aniline and *p*-toluidine, although similar treatment of 1-nitroanthraquinone leads to the formation of phenyl- and *p*-tolyl-aminoanthraquinones. Many arylamino derivatives of anthraquinones have thus been obtained and described mostly in the patent literature (D.R.P., 235, 776; 113, 011; 137,566; 126,542; 127,458; 127,459; 127,438; 106,227; 108,420). The preparation of anthraquinone violet involves such a replacement of nitro groups by arylamino groups. It is obtained by heating 1:5-dinitroanthraquinone with *p*-toluidine and sulphoning the product.

The action of primary aromatic amines on hydroxy-nitroanthraquinones has also been studied. In these cases, it is found that the nitro group is preferentially replaced by the arylamino group (Baeyer, D.R.P., 127,438). Thus, 4:8 dinitroanthrarufin gives with  $\text{R-NH}_2$  the following derivative:



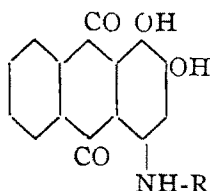
Similarly, it is known that in the case of 5-nitroquinazarin, aniline reacts first with the nitro group and then with the hydroxyl group (J. Houben and W. Fische, "Das Anthracen und Anthrachinon", p. 426).

However, the reaction with the nitro group has been found to be particularly selective at temperatures between  $100^\circ$  and  $150^\circ$ , while the hydroxyl group reacts with the amines only above  $150^\circ$  (Lassar-Cohn-Arbeits-Methoden Ed.V, pp. 456-7).

Lastly, it is found that a nitro group in *para* position to a hydroxyl group is specially reactive and the condensation with primary arylamines takes place with ease, and even in absence of a condensation agent (cf. J. Houben and W. Fische, *ibid.*, p. 427).

A few arylamino derivatives of alizarin have now been obtained by condensing 4-nitroalizarin with the following primary aromatic amines (a) aniline, (b) *o*-nitroaniline, (c) *p*-nitroaniline, (d) *m*-nitroaniline, (e) *p*-toluidine, (f)  $\alpha$ -naphthylamine, (g)  $\beta$ -naphthylamine.

The general structural formula for the arylamino derivatives obtained is represented by,



(where R=aryl or substituted aryl or naphthyl residue), and is based on the following evidence :—

(a) The analytical results show that the nitrogen content corresponds to the presence of one and only one arylamino residue introduced into the alizarin molecule. This excludes the possibilities wherein one of the hydroxyl groups is replaced by the arylamino group. (These products would contain an additional N atom as  $\text{NO}_2$  )

(b) The possibility that the condensation product might carry an arylamino group in the *meso* position is also ruled out as these products have been subjected to alkaline hydrolysis which is known to eliminate such groups in *meso* position (Barry-Barnett, "Anthracene", p. 202).

(c) Lastly, the presence of two free hydroxyl groups is indicated by the solubility of the products in alkali and the formation of a crystalline dibenzoyl derivative in the case of each of the products.

The arylamino compounds obtained with the three nitroanilines and carrying a  $\text{NO}_2$  group were reduced with zinc and 50% acetic acid to the corresponding amino derivatives. The benzoyl derivatives of these arylamino compounds have been obtained. The dyeing properties of the arylamino derivatives of alizarin and of their benzoyl derivatives have been studied. The former were used as mordant dyes (Al-mordant) and the latter as vat dyes. The vatting was effected with hydrosulphite in a dilute solution of sodium silicate at  $40^\circ$ .

The dyeing tests thus indicate that the introduction of arylamino and nitroarylamino residues into the alizarin molecule does not enhance its tinctorial property although the nitroarylamino derivatives give brighter shades than those obtained with the arylamino derivatives.

It is known that sulphonation of these compounds would give rise to dyes with powerful tinctorial properties. Work in this connection is being carried out and is in progress in our laboratory.



## EXPERIMENTAL

*Preparation of the Arylamino Derivatives.*—The arylamino derivatives were all obtained by the following general method, with minor variations. An intimate mixture of 4-nitroalizarin (5 g.), dry boric acid (4 g.) and an excess of the amine was heated with an air condenser on an oil-bath at  $120^{\circ}$  for 8 hours. The reaction mixture was then cooled and treated with dilute HCl, boiled and filtered. The treatment with boiling hydrochloric acid was repeated till the excess of the amine was completely removed. The residue was then dissolved in 30 ml of warm 5% NaOH and reprecipitated with dilute HCl. It was finally washed with water till free of the acid, dried and crystallised twice from pyridine.

*4-Phenylaminoalizarin (I)* was obtained by condensing 4-nitroalizarin with aniline by the procedure described above. It formed dark brown needles, m.p.  $215^{\circ}$ , yield 61%. It is insoluble in dilute mineral acids. With concentrated  $H_2SO_4$  it gives a red solution. Its solution in NaOH is violet. An 1% dye shade was obtained on cotton mordanted with alum; it was deep violet (Found. C, 72.92; H 4.01; N, 4.37.  $C_{20}H_{13}O_4N$  requires C, 72.51; H, 3.94; N, 4.23 per cent).

*4-Phenylaminodibenzoylalizarin.*—The above compound (I, 3 g.) was intimately mixed with 3 g. of fused sodium acetate and the mixture added to 30 ml of hot nitrobenzene; 5 ml. of benzoyl chloride were then added and the whole refluxed on a sand-bath for 6 hours. On cooling, the dibenzoyl derivative separated out. It was filtered and washed with petrol till free of nitrobenzene and then boiled with water several times to remove Na acetate and benzoic acid, and finally crystallised from benzene as brown needles, m.p.  $198^{\circ}$ , yield 64%.

It gives a blood-red solution with  $H_2SO_4$  (conc.). Warm NaOH hydrolyses it and gives a violet coloured solution. With "hydros" in dilute solution of  $Na_2SiO_3$  at  $40^{\circ}$ , it gave a pink vat. A pale violet dye shade was obtained after dyeing. (Found: C, 75.21; H, 4.11; N, 2.57.  $C_{34}H_{21}O_6N$  requires C, 75.70; H, 3.90; N, 2.60 per cent).

*4-(p-Tolyl)-aminoalizarin (II)* was obtained by condensing 4-nitroalizarin with *p*-toluidine. It formed brown needle shaped crystals, m.p.  $204^{\circ}$ , yield 67%. It is insoluble in dilute acids. With  $H_2SO_4$  (conc.) a reddish brown solution is obtained. With NaOH it gives a violet coloration. It is soluble in alcohol and acetic acid. An 1% dye shade was obtained on cotton mordanted with Al, which gave a brownish violet shade. (Found: C, 73.63; H, 4.49; N, 4.33.  $C_{21}H_{16}O_4N$  requires C, 73.04; H, 4.35; N, 4.06 per cent).

*4-(p-Tolyl)-aminodibenzoylalizarin* was obtained by the benzoylation of (II) by the procedure adopted in the case of (I). It formed light brown needles, m.p.  $239^{\circ}$ , yield 69%. With  $H_2SO_4$  (conc.) it gives a red solution; warm NaOH produces a violet solution. On reduction with "hydros" in dilute  $Na_2SiO_3$  solution at  $40^{\circ}$  a pink vat was obtained. A pale violet dye shade was obtained after dyeing (Found: C, 75.83; H, 4.25; N, 2.74.  $C_{38}H_{28}O_6N$  requires C, 75.95; H, 4.16; N, 2.53 per cent).

*4-(o-Nitrophenyl)-aminoalizarin (III)* was obtained by the condensation of 4-nitroalizarin with *o*-nitroaniline as described above. It formed orange coloured prisms, m.p.  $272^{\circ}$ , yield 60%.

It is insoluble in dilute acids. With  $\text{H}_2\text{SO}_4$  (conc.) it forms a deep orange solution; it dissolves in NaOH with a blue colour. An 1% dye shade was obtained on cotton mordanted with Al. A pink dye shade was developed. (Found: C, 64.01; H, 3.32; N, 7.56.  $\text{C}_{20}\text{H}_{12}\text{O}_6\text{N}_2$  requires C, 63.83; H, 3.19; N, 7.45 per cent).

4-(*o*-Nitrophenyl)-aminodibenzoylizarin was obtained by the benzoylation of (III) by the procedure as under (I). It formed golden yellow needles, m.p.  $257^\circ$ , yield 61%. With  $\text{H}_2\text{SO}_4$  (conc.) it forms a brown solution; warm NaOH gives a blue solution. With 'hydros' in a weakly alkaline solution, it gives a reddish brown vat. A brownish red shade was obtained after dyeing. (Found: C, 70.12; H, 3.39; N, 4.72.  $\text{C}_{34}\text{H}_{20}\text{O}_8\text{N}_2$  requires C, 69.86; H, 3.42; N, 4.79 per cent).

4-(*o*-Aminophenyl)-aminoalizarin was obtained by reduction of (III). The compound (III, 5 g.) was added to 60 ml. of 50% acetic acid and then 3 g. of Zn dust. The reduction was allowed to proceed for 2 hours. Dilute HCl (40 ml.) was then added to the reaction mixture to dissolve the excess of Zn. On dilution with water, the amino compound separated out; it was filtered, washed at the pump with water, dried and crystallised from alcohol, as red needles, m.p.  $221^\circ$ , yield 75%.

It dissolves in  $\text{H}_2\text{SO}_4$  (conc.) giving a dark red solution. It is also soluble in NaOH with violet coloration. An 1% shade was obtained on cotton mordanted with Al. A light pink shade was obtained. (Found: C, 69.31; H, 4.16; N, 8.20.  $\text{C}_{20}\text{H}_{14}\text{O}_4\text{N}_2$  requires C, 69.36; H, 4.05; N, 8.09 per cent).

4-(*m*-Nitrophenyl)-aminoalizarin (IV) was obtained by condensing 4-nitroalizarin with *m*-nitroaniline as described under (I). It formed light red needles, m.p.  $269^\circ$ , yield 72%. It is insoluble in dilute mineral acids. With  $\text{H}_2\text{SO}_4$  (conc.) a light brown solution is formed. NaOH solution gives a blue coloration. An 1% dye shade was obtained on cotton mordanted with Al. A pink dye shade was obtained. (Found: C, 63.98; H, 3.10; N, 7.27.  $\text{C}_{20}\text{H}_{12}\text{O}_6\text{N}_2$  requires C, 63.83; H, 3.19; N, 7.45 per cent).

4-(*m*-Nitrophenyl)-aminodibenzoylizarin was obtained by the benzoylation of (IV) as in the case of (I). It formed yellow needles, m.p. above  $310^\circ$ , yield 63%. With  $\text{H}_2\text{SO}_4$  (conc.) it gives a brown solution. It dissolves in warm NaOH with a blue solution. On reduction with 'hydros' it gives a reddish brown vat. A brownish red shade was obtained after dyeing. (Found: C, 70.0; H, 3.51; N, 4.91.  $\text{C}_{34}\text{H}_{20}\text{O}_8\text{N}_2$  requires C, 69.86; H, 3.42; N, 4.79 per cent).

4-(*m*-Aminophenyl)-aminoalizarin was obtained by the reduction of (IV) with Zn and 50% acetic acid as in the case of (III). It formed deep orange coloured needles, m.p.  $235^\circ$ , yield 72%. It does not dissolve in dilute mineral acids, but is soluble in warm acetic acid giving a red solution. It is soluble in NaOH solution with a violet coloration. With  $\text{H}_2\text{SO}_4$  (conc.) it gives a dark red solution. An 1% dye shade was obtained on cotton mordanted with Al. It gave a light pink shade. (Found: C, 69.08; H, 4.17; N, 7.96.  $\text{C}_{20}\text{H}_{14}\text{O}_4\text{N}_2$  requires C, 69.36; H, 4.05; N, 8.09 per cent).

4-(*p*-Nitrophenyl)-aminoalizarin (V) was obtained by condensing 4-nitroalizarin with *p*-nitroaniline as described above. It formed orange needles, m.p.  $253^\circ$ , yield 75%. It is insoluble in dilute mineral acids but dissolves in acetic acid. With  $\text{H}_2\text{SO}_4$  (conc.)

it gives a brown solution, and with NaOH a violet solution. An 1% dye shade was obtained on cotton mordanted with Al. A red shade was obtained. (Found : C, 64.02 ; H, 3.28 ; N, 7.59.  $C_{20}H_{12}O_6N_2$  requires C, 63.83 ; H, 3.19 ; N, 7.45 per cent).

4-(*p*-Nitrophenyl)-aminodibenzoylizarin was obtained by the benzylation of (V) as in the case of (I). It formed yellow plates, m.p. 282°, yield 65%. With  $H_2SO_4$  (conc.) it gives a reddish brown solution; it dissolves in warm NaOH solution with a blue colour. Reduction with 'hydros' gives a reddish brown vat. Mercerised cotton dyed in a 2% dye bath gave a brownish red dye shade. (Found: C, 69.41 ; H, 3.75 ; N, 4.70.  $C_{34}H_{20}O_8N_2$  requires C, 69.86 ; H, 3.42 ; N, 4.79 per cent).

4-(*p*-Aminophenyl)-aminoalizarin was obtained by the reduction of (V) as in the case of (III). It formed red prisms, m.p. 185-87°, yield 78%. With  $H_2SO_4$  (conc.) it forms a blood-red solution; it dissolves in NaOH solution with a violet colour. An 1% dye shade was obtained with cotton mordanted with Al. A light pink shade was obtained. (Found: C, 69.22 ; H, 4.17 ; N, 7.88.  $C_{20}H_{14}O_4N_2$  requires C, 69.36 ; H, 4.05 ; N, 8.09 per cent).

4-( $\alpha$ -Naphthyl)-aminoalizarin (VI) was obtained by condensing 4-nitroalizarin with  $\alpha$ -naphthylamine as described under (I). It formed greenish yellow prisms, m.p. 219°, yield 75%. It is insoluble in dilute mineral acids. With  $H_2SO_4$  (conc.) it gives a deep red solution. It is soluble in NaOH solution with a violet coloration. An 1% dye shade was obtained on cotton mordanted with Al. A pink shade was obtained. (Found : C, 75.68 ; H, 3.83 ; N, 3.79.  $C_{24}H_{18}O_4N$  requires C, 75.60 ; H, 3.94 ; N, 3.67 per cent).

4-( $\alpha$ -Naphthyl)-aminodibenzoylizarin was obtained by the benzylation of (VI) as in the case of (I). It formed brown plates, m.p. 240°, yield 62%. With  $H_2SO_4$  (conc.) it gives a deep red solution. It dissolves in warm NaOH solution with violet colour. On reduction with 'hydros' in weakly alkaline solution it gave a blue vat. A violet dye shade was obtained. (Found: C, 77.58 ; H, 3.81 ; N, 2.49.  $C_{38}H_{22}O_8N$  requires C, 77.42 ; H, 3.90 ; N, 2.38 per cent).

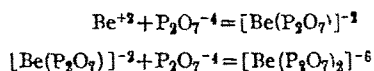
4-( $\beta$ -Naphthyl)-aminoalizarin (VII) was obtained by condensing 4-nitroalizarin with  $\beta$ -naphthylamine as described under (I). It formed reddish brown needles, m.p. 227°, yield 70%. It is insoluble in dilute mineral acids. With  $H_2SO_4$  (conc.) it gives a blood red solution; in warm NaOH solution a blue colour is developed. An 1% dye shade was obtained on cotton mordanted with Al. The dye shade was pink. (Found : C, 75.79 ; H, 4.06 ; N, 3.62.  $C_{24}H_{18}O_4N$  requires C, 75.60 ; H, 3.94 ; N, 3.67 per cent).

4-( $\beta$ -Naphthyl)-aminodibenzoylizarin was obtained by the benzylation of (VII) as in the case of (I). It formed brown prisms, m.p. 302°, yield 60%. With  $H_2SO_4$  (conc.) a red solution is formed. It dissolves in warm NaOH giving a violet solution. Reduction with 'hydros' in a weakly alkaline solution gives a bluish violet vat. A 2% dye shade on mercerised cotton gave a violet shade. (Found: C, 77.63 ; H, 3.78 ; N, 2.29.  $C_{38}H_{22}O_8N$  requires C, 77.42 ; H, 3.90 ; N, 2.38 per cent).

## PHYSICO-CHEMICAL INVESTIGATION ON THE COMPLEX FORMATION BETWEEN PYROPHOSPHATE ION AND BERYLLIUM ION IN SOLUTION

BY BARUN CHANDRA HALDAR

The complex formation between pyrophosphate ion and beryllium ion has been studied in solution by different physico-chemical methods such as transport, thermometric, conductometric,  $p_H$ -measurements and cryoscopy in saturated sodium sulphate solutions. It has been proved conclusively that in solution containing excess of alkali pyrophosphate and beryllium salt, anionic complex ions having beryllium in the anion are present. The complex ions are of the type  $[\text{Be}(\text{P}_2\text{O}_7)]^{-2}$  and  $[\text{Be}(\text{P}_2\text{O}_7)_2]^{-6}$  and are found to exist in simple monomeric form. In presence of excess of pyrophosphate ion, the complex formation may be represented in a stepwise manner as follows :



The early attempt to prepare sodium beryllium pyrophosphate was made by Persoz (*Annalen*, 1848, **64**, 174). Atterberg (*Svenska Akad. Handb.*, 1873, **12**, 34) observed the solubility of beryllium pyrophosphate in sodium pyrophosphate solution and found that two molecules of sodium pyrophosphate can take up more than one molecule of beryllium pyrophosphate. The solution of beryllium pyrophosphate in excess of sodium pyrophosphate does not give the test of beryllium ion. When the solution is, however, boiled with nitric acid, the presence of beryllium ion is indicated by ammonia, ammonium sulphide and sodium carbonate. It shows that in excess of sodium pyrophosphate solution beryllium ion forms complex ion or ions with pyrophosphate ion. But no definite evidence has been put forward upto now in its favour. Even the literature on sodium beryllium pyrophosphate does not record any physico-chemical investigation on the nature of beryllium complexes present in excess of pyrophosphate solution.

The reaction between pyrophosphate ion and beryllium ion has been studied from the standpoint of physico-chemical properties of the mixed solutions by methods such as transport, thermometric, conductometric,  $p_H$ -measurements and cryoscopy in saturated sodium sulphate solution.

### EXPERIMENTAL

#### *Transport Measurements*

The apparatus used is due to Duval (*Bull. soc. chim.*, 1938, **v**, **5**, 1020). It consists of a U-shaped glass tube of 12 cm. in height and 6 mm. (internal diameter) bore. The two branches of the glass tube are provided with two stop-cocks. The stop-cocks are fitted without any grease and do not allow normal diffusion. A third branch is attached at the centre of the base of the glass tube. The experimental liquid can be introduced in the curved portion of the glass tube without opening the stop-

cocks through this branch. It also makes the apparatus stable. The branches above the stop-cocks contain an indifferent electrolyte. They are then connected through a commutator to 105 volts (D.C.). The current is passed for 10 minutes to 4 hours as the case may be. The electrolyte in the branches above the stop-cocks were analysed both qualitatively and quantitatively after the passage of the electric current. The process was repeated by changing the direction of the current. Experiments with colloidal particles should not be made with this apparatus because the colloidal particles choke the capillary passage of the stop-cocks. The current should not be passed for such a long period of time as to allow the diffusing ions under electric current to reach the electrode surface. In that case secondary reaction will take place at the electrode surfaces and the true result may not be obtained. The stop-cocks are freshly grinded usually after use for three to four months. Otherwise diffusion, when no current is passing, will take place. In order to see whether diffusion takes place or not, when stop-cocks are closed and no current is passing, distilled water is kept in the portion below the stop-cocks and hydrochloric acid is taken in the branches above the stop-cocks. After 24 hours, the distilled water is taken out through the third branch and is tested for chloride.

The solution containing excess of sodium pyrophosphate and beryllium sulphate is placed in the glass tube below the stop-cocks through the third branch. The stop-cocks are kept closed. A very dilute solution of sodium chloride is taken in the two branches above the stop-cocks. Electric current is passed for 30 minutes. The solution of the anode branch is taken out and heated with a few drops of nitric acid. It is then evaporated to dryness. The residue is taken with water and tested for beryllium with quinalizarine. Beryllium was found in the anode. The direction of the current was reversed and again beryllium was found in the anodic liquid. A blank test with the dilute solution of sodium chloride used was also performed and beryllium was found to be absent. It proves without any ambiguity that in solutions containing excess of sodium pyrophosphate and beryllium sulphate, beryllium ion is present as anionic complex ion.

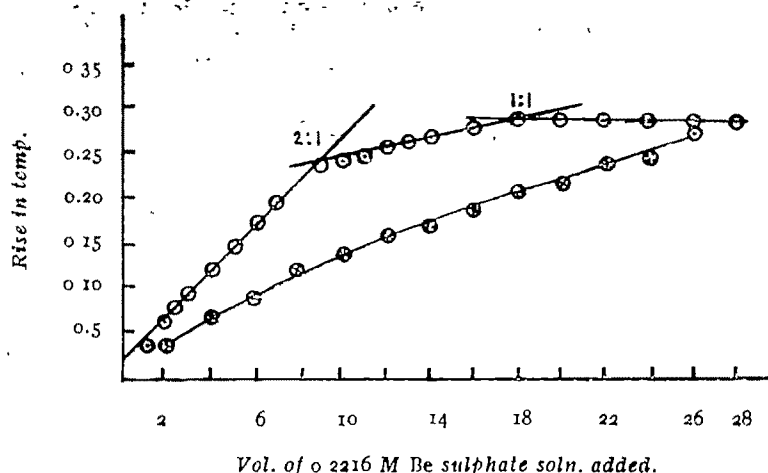
#### *Thermometric Measurements*

The thermometric apparatus is the same as that already described by the author (this *Journal*, 1946, 23, 57) in a previous paper.

The reagents used were of A.R. quality. Standard solution of sodium pyrophosphate was prepared by direct weighing in a chemical balance. The strength of sodium pyrophosphate solution was, however, checked by converting the pyrophosphate into phosphate and then estimating the total phosphate as magnesium pyrophosphate. Potassium pyrophosphate used was prepared from anhydrous dipotassium hydrogen phosphate by the method of Kolthoff and Walters (*Ind. Eng. Chem. Anal. Ed.*, 1943, 15, 8). Standard solutions of potassium pyrophosphate was prepared by estimating the total phosphate of the solution as already stated. Beryllium was estimated as beryllium oxide ( $\text{BeO}$ ).

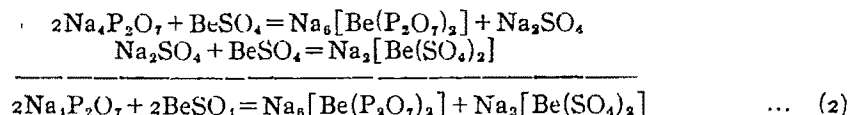
The thermometric titration results are shown graphically in Figures 1 to 3 and are discussed below.

FIG. 1



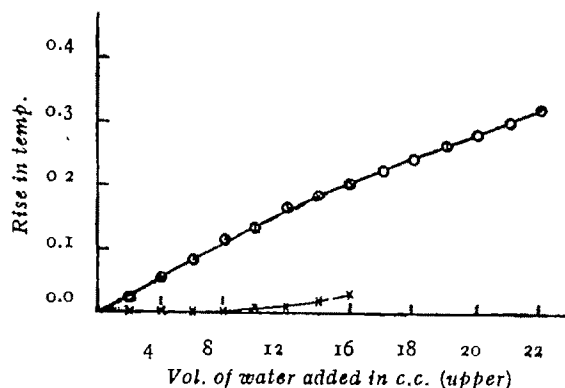
Upper curve refers to 40 c.c. of 0.1 M-Na pyrophosphate soln. and the lower one to 40 c.c. of water.

The thermometric titration curves of alkali pyrophosphate with beryllium sulphate and *vice versa* give two breaks corresponding to the complex ions of the type  $[\text{Be}(\text{P}_2\text{O}_7)_2]^{-6}$  and  $[\text{Be}(\text{P}_2\text{O}_7)]^{-2}$ , taking the simplest values of the ratios. The break due to the formation of normal beryllium pyrophosphate is shown in Fig. 3. The second break in Fig. 1 may also be explained as due to the formation of complex sulphates according to the following equation:



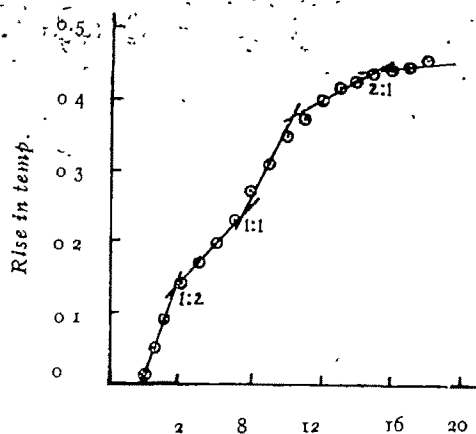
(Literature on double sulphates of beryllium and sodium show that compound of the above formula does exist). Now if the point pyro : beryllium = 1 : 1 be due to the complex ion  $[\text{Be}(\text{SO}_4)_2]^{-2}$  and not due to  $[\text{Be}(\text{P}_2\text{O}_7)]^{-2}$ , then the titration curve of beryllium sulphate with potassium pyrophosphate would have been different. For, in this case beryllium pyrophosphate is precipitated first and the corresponding amount of potassium sulphate is produced. Now in the solution there is not enough beryllium sulphate present to react with potassium sulphate to form the complex ion  $[\text{Be}(\text{SO}_4)_2]^{-2}$  and so the break at the point pyro : beryllium = 1 : 1 would not appear. But experimentally it is found otherwise. If, however, both the complex ions  $[\text{Be}(\text{SO}_4)_2]^{-2}$  and  $[\text{Be}(\text{P}_2\text{O}_7)]^{-2}$  are formed simultaneously, then the second break in Fig. 1 would have been shifted to the higher value of beryllium sulphate concentration. Since no such shift is observed, it may be concluded that the stability of the complex ion  $[\text{Be}(\text{SO}_4)_2]^{-2}$  (provided it exists) must be very much less than that of the ion  $[\text{Be}(\text{P}_2\text{O}_7)]^{-2}$ , so that at the point pyro : beryllium = 1 : 1, the complex ion  $[\text{Be}(\text{P}_2\text{O}_7)]^{-2}$  predominates and the reaction between pyrophosphate ion and beryllium ion may be considered to be the main reaction. The third break in Fig. 3 is

FIG. 2



Upper curve refers to 40 c.c. of 0.2 M-Na-pyrophosphate soln. and lower one to 40 c.c. of water.

FIG. 3



The curve refers to 40 c.c. of 0.2216 M Be sulphate soln.

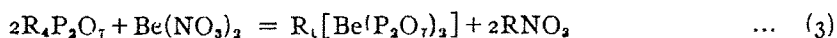
probably due to the mixture of two compounds  $K_2[Be(P_2O_7)]$  and  $K_6[Be(P_2O_7)_2]$  and does not correspond to any definite compound formation. For no such break appears in the titration curve of sodium pyrophosphate with beryllium sulphate solution

### Conductivity Measurements

The conductivity apparatus consists of a box type conductivity bridge of Leeds and Northrup Co., Philadelphia, U.S.A. An audio-frequency oscillator is used as a sound source and a visual indicator served for the detection of the null point.

The conductivity titrations of alkali-pyrophosphates were made with beryllium nitrate solution and are shown in Fig. 4. The conductance-composition curves were drawn from measurements with sodium pyrophosphate and beryllium sulphate solutions.

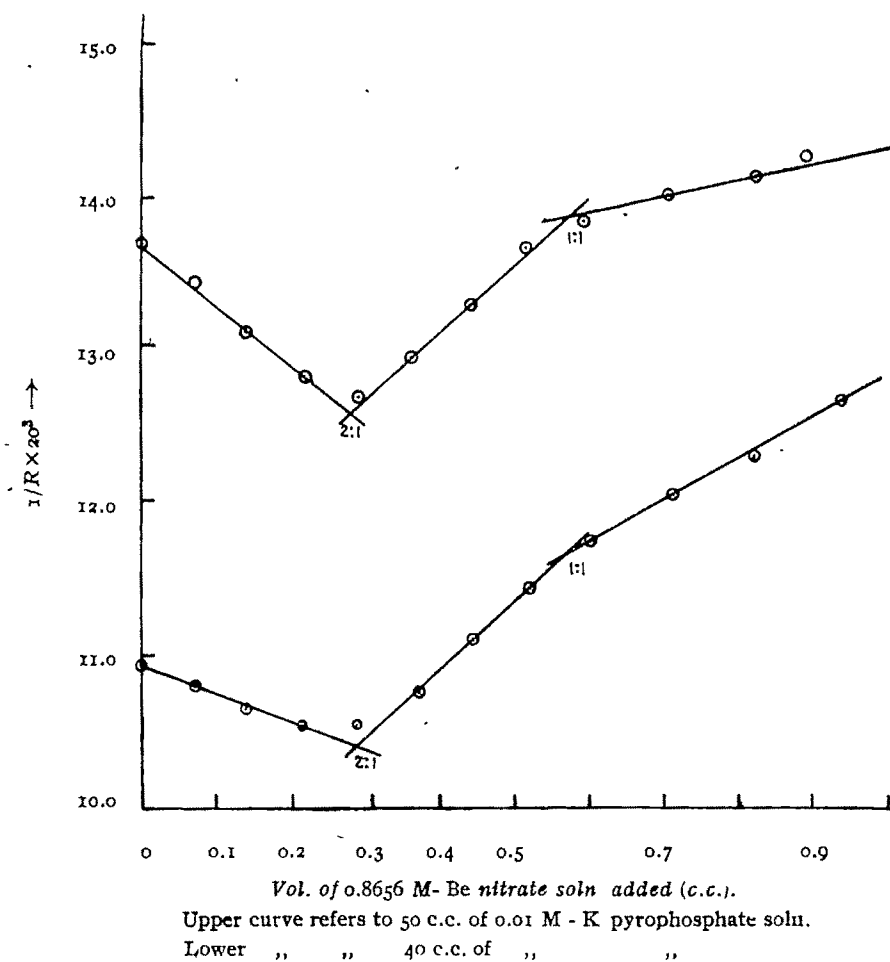
The conductometric titration curves support the thermometric results already stated. The conductance of the alkali pyrophosphate solutions decreases with the addition of beryllium nitrate solution up to the point pyro : beryllium = 2 : 1. After this point the slope of the curve changes sharply indicating the formation of the complex ion  $[Be(P_2O_7)_2]^{-6}$ . The total reaction in solution may be represented as



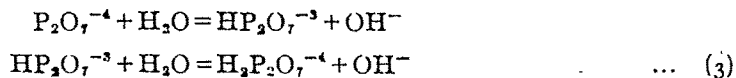
when  $R = Na$  or  $K$ .

But from the above equation, the fall in conductance of alkali pyrophosphate solutions with addition of beryllium nitrate solution up to the point pyro : metal = 2 : 1 cannot be explained. Due to the formation of the complex ion  $[Be(P_2O_7)_2]^{-6}$ , eleven ions are produced for every ten ions present in the solution. It can, however, be accounted for by supposing that the formation of the complex ion  $[Be(P_2O_7)_2]^{-6}$  is attended with suppression of hydrolysis of alkali pyrophosphate solution. This is expected

FIG. 4



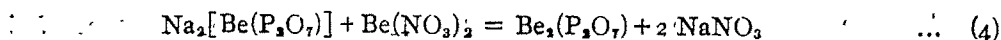
to be so. For in alkali pyrophosphate solution an equilibrium of the type



exists. If, however, free pyrophosphate ion is removed from the system, as in the complex formation between beryllium ion and the pyrophosphate ion, the equilibrium relation of (3) is shifted towards the left. That is, the concentration of free hydroxyl ion, an ion with very high ionic mobility compared to the other ions present, decreases in the solution. The net effect is observed in the lowering of the conductance of the alkali pyrophosphate solutions with the addition of beryllium nitrate solution, although total number of ions increases in the solution. This process continues up to the point pyro : beryllium = 2 : 1. The conductance of the alkali pyrophosphate solutions increases sharply after the point pyro : beryllium = 2 : 1. This is due to the for-



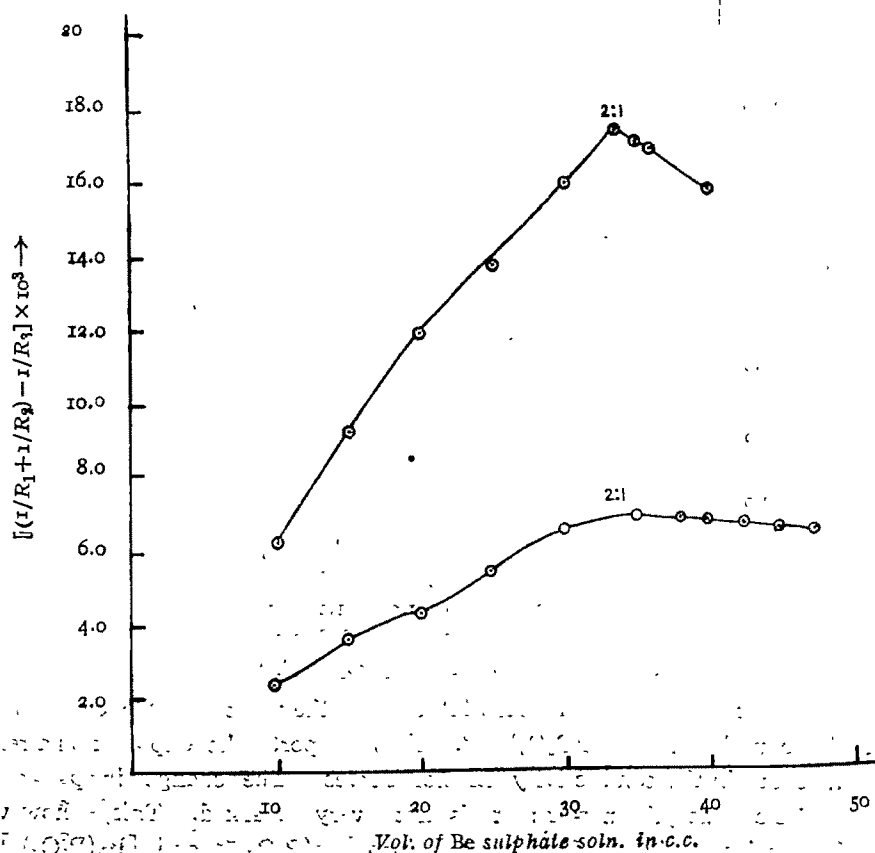
mation of the complex ion  $(\text{BeP}_2\text{O}_7)^{-2}$  in increasing concentration. Because, with its formation ten ions are produced for every seven ions present in the solution, and hence increase in the conductance is observed. The rate of change of conductance takes place linearly up to the point pyro : beryllium = 1 : 1. At this point the rate of increase in the conductance decreases. It may be explained as follows: After the point pyro : beryllium = 1 : 1, beryllium pyrophosphate is produced according to the following equation :



In the present case four ions are produced for every three ions present in the solution and so the conductance of the solution increases. But the rate of change of conductance, after the point pyro : beryllium = 1 : 1 is, however, less than that before it.

For equimolecular solutions, the conductance-composition curves (Fig. 5) of sodium pyrophosphate and beryllium sulphate solutions show maxima at the point pyro : beryllium = 2 : 1. The maxima is found to be independent of the concentrations of the reactants used and therefore gives true composition of the compound formed. Hence

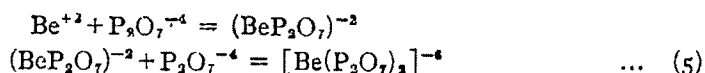
FIG. 5



Upper curve refers to Be sulphate = 0.09533 M and Na pyrophosphate soln. = 0.0533 M.

Lower curve refers to Be sulphate = 0.02 M and pyrophosphate = 0.02 M.

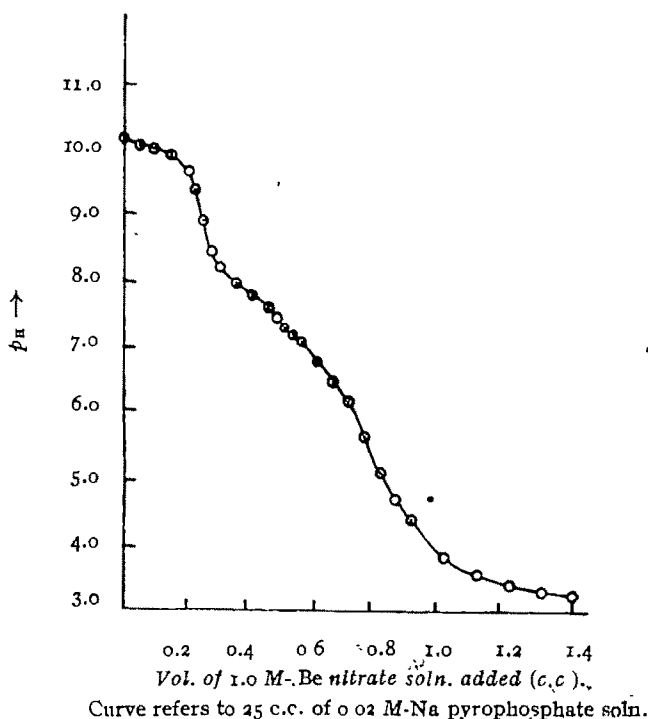
the complex ion is  $[\text{Be}(\text{P}_2\text{O}_7)_2]^{-6}$ . The reaction between pyrophosphate ion and beryllium ion may thus be supposed to take place as follows :



#### *p<sub>H</sub> Measurements*

The  $p_H$  measurements were made with a Beckmann  $p_H$ -meter model G of National Technical Laboratories, South Pasadena, California. Solutions containing the same amount of sodium pyrophosphate and different amounts of beryllium nitrate solutions were prepared. The  $p_H$  of these solutions were then measured with Beckmann  $p_H$ -meter. The corrections in the  $p_H$  values due to the presence of a large excess of sodium ions in the solutions were made with the help of a chart supplied with the instrument. The corrected  $p_H$  were then plotted against the concentrations of beryllium nitrate used and the graph (Fig. 6) obtained.

FIG. 6



The  $p_H$ -titration curve indicates a sharp fall in  $p_H$  at the point corresponding to the formation of the complex ion  $[\text{Be}(\text{P}_2\text{O}_7)_2]^{-6}$ . This supports the explanation already given for the initial fall in the conductivity titration curves. The change in  $p_H$  at the point pyrophosphate : beryllium = 1 : 1 is not very marked. This, however, depends upon the relative stabilities of the complex ions  $[\text{Be}(\text{P}_2\text{O}_7)]^{-2}$  and  $[\text{Be}(\text{P}_2\text{O}_7)_2]^{-6}$ . After the point representing normal beryllium pyrophosphate, the  $p_H$  of the solution changes slowly with the addition of beryllium nitrate solution.

*Cryoscopy Measurements in Saturated Sodium Sulphate Solution*

From the preceding investigations it has been definitely proved that in a solution containing excess of sodium pyrophosphate and beryllium salt, two complex ions, in which the ratios of pyro : beryllium are 2 : 1 and 1 : 1, exist. It has been tacitly assumed that the above complex ions exist in simple monomeric form in solution. But no direct evidence has been cited in its favour. The cryoscopy in saturated sodium sulphate solution is expected to throw some light on this matter.

Cryoscopy in saturated sodium sulphate solution is due to Darmois (*Bull. soc. chim. Belg.*, 1927, 86, 64). The apparatus consists of a 200 c.c. beaker placed inside a Dewar flask over an insulating material ; 50 c.c. of water at about 33° were taken in the beaker. Anhydrous sodium sulphate (30 g.) was added to the water in the beaker. The mouth of the Dewar flask was closed by means of a cover of asbestos sheet, provided with three bores, one for passing a mechanical stirrer driven by a motor and another for introducing a Beckmann thermometer. The solution was allowed to cool and as soon as the mercury thread passed the point corresponding to the transition point between the decahydrate and the anhydrous sodium sulphate, some quantity of Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) was added to the beaker by the third opening. After a little recalescence phenomenon, the mercury thread began to rise. A stop-watch was started at this point. After 20 minutes (usually) the temperature was found to be constant. It gives the transition point of sodium sulphate in water. The tracing of the cooling curve during the determination of the transition point is found to be unnecessary as it is observed that the temperature attained at the twentieth minute gives the transition temperature accurately.

The maximum recalescence observed by the author is 0.5° even by introducing Glauber's salt as a seeding material and the maximum recorded by others is 1.9°.

It has been reported by Bye (*Bull. soc. chim.*, 1942, 9, 517) that the conversion of 50 g. of water into the solid phase of the hydrated sodium sulphate takes 10 hours. So the amount of water taken up by the anhydrous sulphate to transform into hydrated salt during 20 minutes is small.

The molecular lowering of the transition point can be determined with the help of the formula,

$$K = \frac{M}{m} \times \Delta t \times \frac{50 + V}{100} \quad \dots \text{ (A)}$$

where  $\Delta t$  = observed lowering of the transition point,

$K$  = molecular constant for 100 g. of the solvent,

$M$  = molecular weight of the substance,

$m$  = wt. of the substance taken,

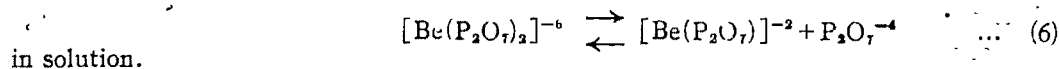
$V$  = volume in c.c. of the added solution.

In the present work 50 c.c. of 0.1M sodium pyrophosphate solution were taken in the beaker. The temperature of the solution was raised by heating to near about 34°. Anhydrous sodium sulphate (30 g.) was added to it. The beaker was then placed inside the Dewar flask and the mouth of the Dewar was closed by the cover. The Beckmann thermometer was introduced into the solution and the mixture was rotated by means of a

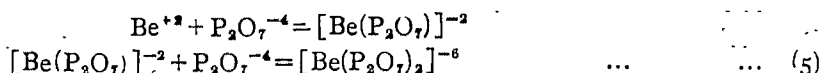
stirrer. Now the calculated amount of beryllium sulphate solution was added to the solution in the beaker so that the ratio of pyro : beryllium = 2 : 1. The transition point of the sodium sulphate was determined as already stated. The temperature was noted. The difference between the two readings, that is when only water is taken and the present gives the observed lowering in the transition point  $\Delta t$ . The value of the constant  $K$  is found out with the help of the equation (A). Comparing the experimental value with that of the theoretical, the molecular form of the complex ion of the type  $[\text{Be}(\text{P}_2\text{O}_7)_2]^{-6}$  is determined.

Quantity of salt used.	Conc. of pyro/conc. of Be	$\Delta t$ .	$K$ .
5.25 c.c. of 0.4772M $\text{BeSO}_4$ soln.	2 : 1	0.1	11.05

The experimentally observed value of the cryoscopy constant is nearly half the value of the molecular constant for single ion (18.2). That is, the number of ions (other than sodium sulphate) present in solution is nearly half the number of pyrophosphate ions used. If it be so, then the complex ion of the type pyro : beryllium = 2 : 1 exists in simple monomeric form as  $[\text{Be}(\text{P}_2\text{O}_7)_2]^{-6}$ . The slightly higher value of the observed constant from that of the theoretical value is explained as due to the existence of equilibrium of the type :



Thus in a solution containing excess of pyrophosphate ion and beryllium ion, the complex ions  $[\text{Be}(\text{P}_2\text{O}_7)_2]^{-6}$  and  $[\text{Be}(\text{P}_2\text{O}_7)]^{-2}$  exist as follows :



The author's best thanks are due to Prof. P. B. Sarkar, Dr. es.Sc., F.N.I., for his keen interest and giving all laboratory facilities during the progress of the work.

INORGANIC CHEMISTRY LABORATORY,  
UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,  
CALCUTTA 9.

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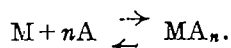
## STABILITY OF COBALTIC BIGUANIDE COMPLEXES

BY ANIL KUMAR DE, NRIPENDRA NATH GHOSH AND PRIYADARANJAN RÂV

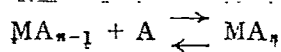
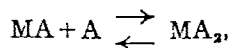
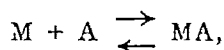
The stability of cobaltic *bis*-biguanide and cobaltic *tris*-phenylbiguanide complexes have been determined from a measurement of the equilibrium constants of their reaction with acids and the acid dissociation constants of the biguanides concerned, together with the determination of the concentration of the cobaltic ion in solution by E.M.F. measurement in a Beckmann  $p_H$ -meter, on the basis of Bjerrum's theory relating to the formation of co-ordinatively saturated complexes by successive stages. The theory has been amply supported by the results obtained.

The individual instability constants  $k_3$ ,  $k_2$  and  $k_1$  for successive stages, as well as the overall constant  $K$ , for biguanide cobaltic complexes have been found to be much smaller than those of the cobaltic ammine complexes and the complexes of other metals, either of simple or inner metallic type. Biguanide cobaltic complexes are thus found to be the most stable of the cationic metal complexes, hitherto examined

In spite of extensive researches for over half a century on co-ordination complexes, culminating recently in the application of the principles of quantum mechanics to account for their structure and behaviour, we are still not in a position to formulate a clear, definite and well-recognized principle guiding the formation of this highly interesting class of compounds. In recent years, however, much attention has been directed by several workers to a quantitative study of the mechanism of formation and stability of these complexes with a view to obtaining greater insight into their character. As a result thereof, much valuable informations about them have already been collected with much more in prospect, which has made possible the occasional preparation of new types of complexes by defining precisely the conditions and range of their existence. Reference may in this connection be made to the comprehensive and pioneering work of Bjerrum ("Metalammine Formation in Aqueous Solution", P. Hasse and Son, Copenhagen, 1941), who has treated the problem on a statistical basis involving the formation of all intermediate stages in a reversible manner. Previous to this, Lamb and Larson (*J. Amer. Chem. Soc.*, 1920, 42, 2024) studied the stabilities of a series of cobaltammines by determining the equilibrium constant for the reversible reaction



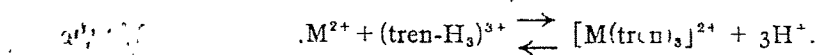
Bjerrum, however, emphasised the importance of the intermediate steps involved in the above overall reaction, viz.,



where M is the metal ion and A, the co-ordinating ligand. The equilibrium constants for the intermediate stages, termed formation constants or consecutive complexity constants by Bjerrum, were thus related to the overall equilibrium constant, or the complexity constant as termed by him. On the basis of Bjerrum's theory of reversible stepwise reactions Carlson, McReynolds and Verhoek (*J. Amer. Chem. Soc.*, 1945, **67**, 1334) investigated the formation of the complexes of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions with ethylenediamine and propylenediamine, and the complexes of  $\text{Ag}^+$  ion with ethyl and diethylamine. The theory has also been applied to the stability of inner metallic complexes by Calvin and Wilson (*ibid.*, 1945, **47**, 2003) in order to make a quantitative survey regarding the influence of certain structural factors upon the stability of chelate complexes of bivalent copper bonded to four oxygen atoms. These copper complexes of *o*-hydroxy aromatic aldehydes and  $\beta$ -diketones are relatively insoluble in water, and hence the measurements had to be made in a water-dioxane (50/50) mixture. As a result of their study on twenty-one chelate compounds of bivalent copper, they attributed the changes in the complexity constant in relation to the structural change in the organic residue to two different force components responsible for binding the copper ion to the chelate residue. One of these was believed to be of the same character for both copper and hydrogen, and the other to be of a quite different nature derived from a resonance effect involving the copper atom.

Mellor and Malcy (*Nature*, 1947, **159**, 370) following the work of Calvin and Wilson (*loc. cit.*) determined the values of formation and complexity constants of inner complexes formed by a series of bivalent metal ions (viz., of Pd, Cu, Ni, Pb, Co, Zn, Cd and Mg) with salicylaldehyde in dioxane-water (50/50) solution. The same authors (*Nature*, 1948, **161**, 436) compared the overall stability constants of the inner metallic complexes of salicylaldehyde-ethylenediamine (a quadridentate chelate molecule), which gave the following order for different metals: Pd, Cu, Ni, Co, Zn, Cd, Fe, Mn, Mg; the values decreasing from left to right. The two series thus show a closely similar order.

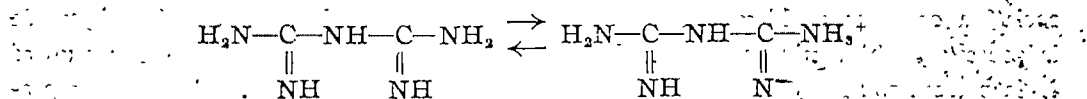
Ackermann, Prue and Schwarzenbach (*Nature*, 1949, **163**, 723) measured the stability constants of the complexes formed by different metal ions with  $\beta\beta'\beta''$ -tri-amino-triethylamine,  $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ , (tren), which behaves as a quadridentate molecule providing four points of attachment for the metal ion. The stability constants were evaluated from the acid dissociation constant of the amine and the equilibrium constant of the reaction



The stability constant values of different metal complexes generally followed the same order as that observed with ammonia or ethylenediamine. The copper complex was, however, found to be less stable than the corresponding ethylenediamine compound, due presumably to factors of steric nature, which renders almost impossible the assumption of a planar configuration.

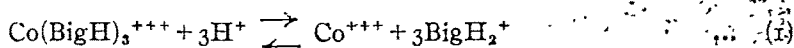
Complex compounds of biguanide and substituted biguanide with metallic elements, which have formed a subject of investigation in this laboratory for several years, belong to the class of inner metallic complexes of the third order (cf. Rây and Dutt,

this *Journal*, 1948, 26, 563) and can give rise to many water-soluble salts. These, therefore, furnish suitable materials for a study of the mechanism of complex formation and the stability of the resulting complexes on the basis of Bjerrum's theory. Biguanide or biguanidinium ion behaves as a bifunctional group occupying two co-ordination positions, while a dibiguanide or its ion functions as a quadridentate group occupying four co-ordination positions. In the present paper we shall describe the results of our study on cobaltic *tris*-biguanide and cobaltic *tris*-phenylbiguanide complexes. The procedure adopted for the purpose, however, differs somewhat from those of the previous workers in view of the nature of the complexes concerned. The biguanide molecule itself possesses a tautomeric structure, each of which again may possess a resonating character :



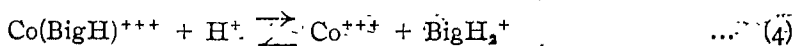
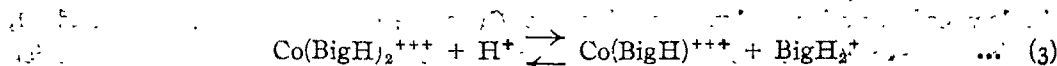
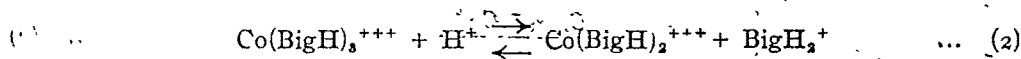
The matter becomes further complicated in the case of a trivalent metal complex like that of cobalt.

The method adopted was as follows. The decomposition of the cobaltic *tris*-biguanide complex was studied in the presence of acid and the equilibrium constant of the reaction was determined. The overall reaction in the presence of acid can be given by :



where  $\text{BigH}_2^+$  represents a biguanidinium ion.

The reaction in fact proceeds in three successive stages as shown below :



The successive equilibrium constants for reactions (2), (3) and (4) are denoted respectively by  $k'_2$ ,  $k'_3$  and  $k'_1$ . These are related to the overall equilibrium constant  $K'$  given by the reaction (1).

$$\begin{aligned} K' &= \frac{[\text{Co}^{+++}][\text{BigH}_2^+]^3}{[\text{Co}(\text{BigH})_3^{+++}][\text{H}^+]^3} \\ &= \frac{[\text{Co}^{+++}][\text{BigH}_2^+]}{[\text{Co}(\text{BigH})^{+++}][\text{H}^+]} \times \frac{[\text{Co}(\text{BigH})^{+++}][\text{BigH}_2^+]}{[\text{Co}(\text{BigH})_2^{+++}][\text{H}^+]} \\ &\quad \times \frac{[\text{Co}(\text{BigH})_2^{+++}][\text{BigH}_2^+]}{[\text{Co}(\text{BigH})_3^{+++}][\text{H}^+]} \\ &= k'_1 \cdot k'_2 \cdot k'_3 \quad (5) \end{aligned}$$

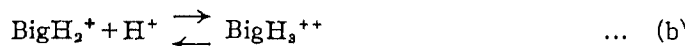
The values of  $[\text{Co}^{+++}]$ ,  $[\text{BigH}_2^+]^3$ ,  $[\text{H}^+]^3$  and  $[\text{Co}(\text{BigH})_3^{+++}]$  should therefore be known, in order to obtain  $K'$ .

The concentration of  $\text{Co}^{+++}$  was determined from the well known Nernst equation

$$E = E_0 + \frac{RT}{F} \ln \frac{a_{\text{Co}^{+++}}}{a_{\text{Co}^{++}}},$$

where  $E$  = observed E.M.F. corrected to normal hydrogen electrode;  $E_0$  = standard electrode potential for cobaltic-cobaltous system; and  $a_{\text{Co}^{+++}}$  and  $a_{\text{Co}^{++}}$  are the activities of cobaltic and cobaltous ions in solution. The values of  $E_0$  for cobaltic-cobaltous system is, as given by Lamb and Larson (*loc cit.*), +1.817 volts at 25°, the temperature coefficient being +0.00169 volt.

The concentration of biguanidinium ion,  $\text{BigH}_2^+$ , was evaluated from the acid dissociation constant of biguanide hydrochloride as follows. In acid solution biguanide is present as biguanidinium ion. In low acid concentration a considerable amount of it is present as  $\text{BigH}_2^+$  ion and to a negligible extent as  $\text{BigH}_3^{++}$  ion. The reaction proceeds in two steps:



The acid dissociation constant  $k_1^*$  corresponding to (a) is given by

$$k_1^* = \frac{C_{\text{BigH}} \cdot C_{\text{H}^+}}{C_{\text{BigH}_2^+}} \quad \dots (6)$$

and that corresponding to (b) by

$$k_2^* = \frac{C_{\text{BigH}_2^+} \cdot C_{\text{H}^+}}{C_{\text{BigH}_3^{++}}} \quad \dots (7)$$

At low concentration of hydrogen ion, let  $C_A$  = the concentration of the acid added,  $C'_A$  (from  $a_{\text{H}^+}$ ) = the concentration of the acid after reaction,  $C_B$  = the concentration of the total biguanide.

Then

$$C_A - C'_A = C_{\text{BigH}_2^+};$$

$$C_B = C_{\text{BigH}} + C_{\text{BigH}_2^+}.$$

$$\text{Therefore, } C_{\text{BigH}} = C_B - C_A + C'_A$$

$$\text{Hence } k_1^* = \frac{(C_B - C_A - C'_A) \cdot [\text{H}^+]}{(C_A - C'_A)} \quad \dots (8)$$

At a higher concentration of hydrogen ion,

$$C_A - C'_A = 2C_{\text{BigH}_3^{++}} + C_{\text{BigH}_2^+};$$

$$C_B = C_{\text{BigH}_3^{++}} + C_{\text{BigH}_2^+};$$

$$\text{Hence } C_{\text{BigH}_3^{++}} = C_A - C'_A - C_B, \text{ and } C_{\text{BigH}_2^+} = 2C_B - C_A + C'_A.$$

$$\text{Therefore, } k_2^* = \frac{(2C_B - C_A + C'_A) [\text{H}^+]}{(C_A - C'_A - C_B)} \quad \dots (9)$$

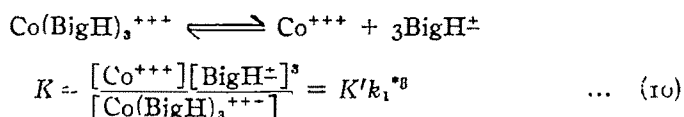
The acid dissociation constants,  $k_1^*$  and  $k_2^*$  of biguanide were thus determined.



The concentration of hydrogen ion  $a_{H^+}$  or  $[H^+]$  in (5) was deduced from the measured  $p_H$  of the acid solution of the complex.

The concentration of  $Co(BigH)_3^{+++}$  was obtained by calculation as shown below.

From these the value of  $K'$  was obtained. The overall instability or dissociation constant  $K$  of the complex is given by :



Now let  $C$  denote the molar concentration of the complex taken and  $C_3, C_2, C_1$  the respective concentrations of  $Co(BigH)_3^{+++}$ ,  $Co(BigH)_2^{+++}$  and  $Co(BigH)^{++}$ , so that

$$C = C_3 + C_2 + C_1 \text{ (neglecting } Co^{+++}) \quad \dots (11)$$

If  $x$  be the total biguanide liberated from the complex then

$$3C - x = 3C_3 + 2C_2 + C_1 \quad \dots (12)$$

The acid consumed in the reaction was obtained from the concentration of the acid added and the final  $p_H$  values of the complex solutions ; the latter was reduced to the acid concentration value from a graph relating the measured  $p_H$  with the negative logarithm of acid concentration (Randall and Young, *J. Amer. Chem. Soc.*, 1928, 50, 989). The difference between this and the concentration of the acid added gave the amount of the acid used up by the reaction with the complex. Let this be denoted by  $Z$ . Evidently,

$$Z = C_{BigH_2^+} + 2C_{BigH_3^{++}} = C_{BigH_2^+} \left( 1 + \frac{2C_{BigH_3^{++}}}{C_{BigH_2^+}} \right) \\ = C_{BigH_2^+} \left( 1 + \frac{2[H^+]}{k_2^*} \right) = C_{BigH_2^+} \left( \frac{k_2^* + 2[H^+]}{k_2^*} \right) \quad \dots (13)$$

Therefore, 
$$C_{BigH_2^+} = \frac{k_2^* Z}{k_2^* + 2[H^+]} \quad \dots (14)$$

Total biguanide liberated from the complex,

$$x = C_{BigH_2^+} + C_{BigH_3^{++}} = C_{BigH_2^+} \left( 1 + \frac{C_{BigH_3^{++}}}{C_{BigH_2^+}} \right) \quad \dots (15) \\ = C_{BigH_2^+} \left( 1 + \frac{[H^+]}{k_2^*} \right) \text{ from (7)} = C_{BigH_2^+} \left( \frac{k_2^* + [H^+]}{k_2^*} \right)$$

Substituting the value of  $C_{BigH_2^+}$  from (14) in (15) we get,

$$x = \frac{Z (k_2^* + [H^+])}{k_2^* + 2[H^+]} \quad \dots (16)$$

Three cases are possible, depending on the relative values of  $x$  and  $C$  :

I. When  $x$  is considerably less than  $C$ , it may be assumed that  $C_1$  present in

the mixture is negligibly small. Equations (11) and (12) are reduced to

$$C = C_3 + C_2 \quad \dots (17)$$

$$\text{and } 3C - x = 3C_3 + 2C_2 \quad \dots (18)$$

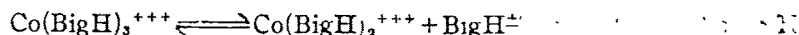
Therefore,  $C_2 = x$  and  $C_3 = C - x$ .

Under this condition only,  $k'_3$  and  $K'$  are obtained:

$$k'_3 = \frac{[\text{Co}(\text{BigH})_2^{++}] [\text{BigH}_2^+]}{[\text{Co}(\text{BigH})_3^{+++}] [\text{H}^+]} = \frac{x}{C-x} \cdot \frac{[\text{BigH}_2^+]}{[\text{H}^+]} \quad \dots (19)$$

$$\text{and } K' = \frac{[\text{Co}^{+++}] [\text{BigH}_2^+]^3}{[\text{Co}(\text{BigH})_3^{+++}] [\text{H}^+]} = \frac{\text{Co}^{+++}}{C-x} \cdot \frac{[\text{BigH}_2^+]^3}{[\text{H}^+]^3} \quad \dots (20)$$

The instability constant  $k_3$ , corresponding to the reaction,



is directly evaluated from  $k'_3$  and  $k_1^*$ .

$$k_3 = \frac{[\text{Co}(\text{BigH})_2^{+++}] [\text{BigH}^+]}{[\text{Co}(\text{BigH})_3^{+++}]} = \frac{[\text{Co}(\text{BigH})_2^{+++}]}{[\text{Co}(\text{BigH})_3^{+++}]} \cdot \frac{k_1^* [\text{BigH}_2^+]}{[\text{H}^+]} \text{ from (6)} \\ \dots (21)$$

So II. When  $x$  is greater than  $C$  but less than  $2C$ ,  $C_3$  present is very small, so that (11) and (12) give

$$C = C_2 + C_1 \text{ and } 3C - x = 2C_2 + C_1 \quad \dots (22)$$

therefore,

$$C_2 = 2C - x \quad \dots (23)$$

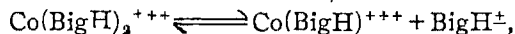
$$\text{and } C_1 = x - C \quad \dots (24)$$

Under this condition only,  $k'_1$  and  $k'_2$  are obtained.

$$k'_2 = \frac{[\text{Co}(\text{BigH})^{+++}] [\text{BigH}_2^+]}{[\text{Co}(\text{BigH})_2^{+++}] [\text{H}^+]} = \frac{x-C}{2C-x} \cdot \frac{[\text{BigH}_2^+]}{[\text{H}^+]} \quad \dots (25)$$

$$k'_1 = \frac{[\text{Co}^{++}] [\text{BigH}_2^+]}{[\text{Co}(\text{BigH})^{+++}] [\text{H}^+]} = \frac{x-C}{2C-x} \cdot \frac{[\text{BigH}_2^+]}{[\text{H}^+]} \quad \dots (26)$$

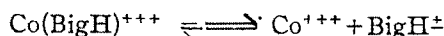
The instability constant  $k_2$  for the reaction,



is obtained from  $k'_2$  and  $k_1^*$ ,

$$k_2 = \frac{[\text{Co}(\text{BigH})^{+++}] [\text{BigH}^+]}{[\text{Co}(\text{BigH})_2^{+++}]} = \frac{[\text{Co}(\text{BigH})^{+++}]}{[\text{Co}(\text{BigH})_2^{+++}]} \cdot \frac{k_1^* [\text{BigH}_2^+]}{[\text{H}^+]} = k'_2 \cdot k_1^* \quad \dots (27)$$

Similarly, the instability constant  $k_1$  corresponding to



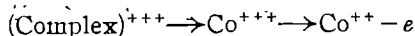
(28) ...

$$k_1 = \frac{[\text{Co}^{+++}] [\text{BigH}^+]}{[\text{Co}(\text{BigH})^{+++}]} = \frac{[\text{Co}^{+++}]}{[\text{Co}(\text{BigH})^{+++}]} \cdot \frac{k_1^* [\text{BigH}_2^+]}{[\text{H}^+]} = k'_1 \cdot k_1^* \quad \dots (28)$$

III. When  $x$  is greater than  $2C$ , both  $C_3$  and  $C_2$  may be regarded as very small, so that (12) gives:

$$C_1 = 3C - x \quad \dots (29),$$

and the fraction  $(C - C_1)/C$  of the complex is almost completely decomposed giving unstable  $\text{Co}^{3+}$  ions, which break up more or less into cobaltous ion in the following manner:



The experimental values of  $k'_1$ ,  $k'_2$  and  $k'_3$  may be compared with the graphical values derived according to the method of Carlson, McReynolds and Verhoek (*loc. cit.*).

$$\bar{n} = \frac{3C - x}{C} = \frac{Y_1[b] + 2Y_1Y_2[b]^2 + 3Y_1Y_2Y_3[b]^3}{1 + Y_1[b] + Y_1Y_2[b]^2 + Y_1Y_2Y_3[b]^3} \quad \dots (30)$$

where  $\bar{n}$  is the ratio of biguanide still remaining in the complex to the concentration of the complex originally taken;

$$Y_1 = 1/k'_1, Y_2 = 1/k'_2, Y_3 = 1/k'_3; \text{ and } [b] = \frac{[\text{BigH}_2^+]}{[H^+]}$$

In this expression,  $Y_1$ ,  $Y_2$  and  $Y_3$  are related to formation constants as defined by Bjerrum (*loc. cit.*).

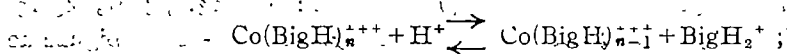
By solving (30) we may get for individual constants

$$Y_1 = \frac{1}{[b]} \times \frac{\bar{n}}{(1 - \bar{n}) + (2 - \bar{n})[b]Y_2 + (3 - \bar{n})[b]^2Y_2Y_3} \quad \dots (31)$$

$$Y_2 = \frac{1}{[b]} \times \frac{(\bar{n} - 1) + \frac{\bar{n}}{[b]Y_1}}{(2 - \bar{n}) + (3 - \bar{n})[b]Y_3} \quad \dots (32)$$

$$Y_3 = \frac{1}{[b]} \times \frac{(\bar{n} - 2) + \frac{(\bar{n} - 1)}{[b]Y_2} + \frac{\bar{n}}{[b]^2Y_1Y_2}}{(3 - \bar{n})} \quad \dots (33)$$

When  $\bar{n} = n - \frac{1}{2}$ , there will be about equal number of  $\text{Co}(\text{BigH})_{n-1}^{++}$  and  $\text{Co}(\text{BigH})_n^{+++}$  ions in the equilibrium mixture



so that as a first approximation,

$$\frac{1}{k'_n} = Y_n = \frac{[\text{Co}(\text{BigH})_{n-1}^{++}][H^+]}{[\text{Co}(\text{BigH})_n^{+++}][\text{BigH}_2^+]} = \frac{[\text{Co}(\text{BigH})_{n-1}^{++}]}{[\text{Co}(\text{BigH})_n^{+++}][b]} = \frac{1}{[b]} \bar{n} = n - \frac{1}{2} \quad \dots (34)$$

Substituting these values in (31), (32) and (33) we get,

$$Y_1 = \frac{1}{[b]_{n=\frac{1}{2}}} \times \frac{1}{1 + 3Y_2[b]_{n=\frac{1}{2}} + 5Y_2Y_3[b]_{n=\frac{1}{2}}^2} \quad \dots (35)$$

$$Y_2 = \frac{1}{[b]_{\bar{n}=\frac{1}{2}}} \times \frac{1 + \frac{3}{Y_1[b]_{\bar{n}=\frac{1}{2}}}}{1 + 3Y_3[b]_{\bar{n}=\frac{1}{2}}} \quad \dots (36)$$

$$Y_3 = \frac{1}{[b]_{\bar{n}=\frac{1}{2}}} \times \left\{ 1 + \frac{3}{Y_2[b]_{\bar{n}=\frac{1}{2}}} + \frac{5}{Y_1 Y_2 [b]_{\bar{n}=\frac{1}{2}}} \right\} \quad \dots (37)$$

The values of  $[b]$  are obtained from the curve drawn by plotting  $\bar{n}$  against  $\log [b]$  or  $p[b]$ . Thus  $Y_1$ ,  $Y_2$  and  $Y_3$  may be obtained approximately from the values of  $[b]$  when  $\bar{n} = \frac{1}{2}$ ,  $\frac{2}{3}$  and  $\frac{3}{4}$  respectively and hence  $k'_1$ ,  $k'_2$  and  $k'_3$  computed.

Similar calculations are applicable to the case of cobaltic *tris*-phenylbiguanidinium chloride.

The mechanism represented here for the dissociation of the cobaltic biguanide complex, strictly speaking, is not a rigid one. For, in solution, complexes of the type  $[\text{Co}(\text{BigH})_2]^{3+}$  and  $[\text{Co}(\text{BigH})]^{3+}$  cannot remain as stable units, but will change readily into hexa-coordinated complexes like  $[(\text{H}_2\text{O})_2.\text{Co}(\text{BigH})_2]^{3+}$  and  $[(\text{H}_2\text{O})_4.\text{Co}(\text{BigH})]^{3+}$  respectively (cf. Rây and Majumdar, this *Journal*, 1946, **24**, 73). In fact, with increase in acidity of the solution the colour of the *tris*-biguanide complex changes from orange to violet-red and that of the *tris*-phenylbiguanide complex from red to dark red. This does not, however, affect our determination, as the concentration of water remains unchanged. In the case of copper *bis*-biguanide complex  $[\text{Cu}(\text{BigH})_2]^{2+}$  it has indeed been possible to isolate the monobiguanide complex,  $[(\text{H}_2\text{O})_2.\text{Cu}(\text{BigH})]^{2+}$  by the addition of a limited amount of an acid (Rây and co-workers, unpublished work).

## EXPERIMENTAL

### Preparation of the Materials

**Biguanide Hydrochloride:**  $\text{C}_2\text{H}_7\text{N}_5.\text{HCl}$  (in solution).—A solution of biguanide monohydrochloride (0.04M) was prepared from a solution of pure recrystallised biguanide acid sulphate by treatment with requisite quantity of KOH solution and barium chloride solution. The solution was filtered from the precipitate of barium sulphate.

**Cobaltic tris-biguanidinium chloride** was prepared and purified according to the method of Rây and Dutt (this *Journal*, 1939, **16**, 623). {Found: Cl, 23.07; N, 45.13.  $[\text{Co}(\text{BigH})_3]\text{Cl}_3$  requires Cl, 22.88; N, 44.85 per cent}. BigH = one biguanide molecule =  $\text{C}_2\text{H}_7\text{N}_5$ .

**Phenylbiguanide Hydrochloride.**—A 0.04M solution of phenylbiguanide hydrochloride was prepared from a pure and freshly recrystallised sample of the substance (cf. Cohn, *J. prakt. Chem.*, 1911, **84**, 394).

**Cobaltic tris-phenylbiguanidinium chloride** was prepared and purified by the method described by Rây and Bhattacharya (this *Journal*, 1939, **16**, 629). {Found: Cl, 14.41; N, 28.20.  $[\text{Co}(\text{PhBigH})_3]\text{Cl}_3 \cdot 2.5 \text{ H}_2\text{O}$  requires Cl, 14.36; N, 28.32 per cent}. PhBigH = one phenylbiguanide molecule,

*Cobalt Chloride.*—A 0.02*M* solution of the substance was prepared from a sample of Kahlbaum's Analar quality and the strength of the solution was adjusted by an analysis of its cobalt content.

*Barium chloride.*—A 0.2*M* solution was prepared from  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$  (Kahlbaum).

*Hydrochloric Acid.*—Chemically pure hydrochloric acid was distilled in an all-glass apparatus. The portion distilling over at a constant boiling temperature was collected. The strength of this solution was determined by titration with standard NaOH solution. From this, solutions of weaker strength were prepared by dilution, whose strengths were further checked by titration against standard NaOH solutions.

All the solutions employed were prepared with conductivity water.

A Beckmann  $p_{\text{H}}$ -meter, model G, was used for  $p_{\text{H}}$  and E. M. F. measurements. The apparatus was previously tested by determining the redox potential of ferrous-ferric system.

*Potassium Hydroxide.*—A 0.337*M* solution was prepared from Merck's guaranteed reagent and its strength determined by titration with standard HCl.

*Acid Dissociation Constants of Biguanide Hydrochloride and of Phenylbiguanide Hydrochloride*

0.04*M*-solution of each was prepared as mentioned above. This hydrochloride solution (12.5 c.c.) was taken in each of four different 50 c.c. volumetric flasks and different amounts of 0.2*M* HCl solution were added to each and then the volume of the solution was made up to the mark. The  $p_{\text{H}}$  values of these solutions were measured by means of the Beckmann  $p_{\text{H}}$ -meter. The acid dissociation constant,  $k^*_{\text{a}}$ , was calculated from eq. (9). The results are given in Tables I and II.

The acid dissociation constant  $k^*_{\text{a}}$  for both the hydrochlorides was calculated by means of eq. (8) from the measurements of Das Sarma (unpublished).

*Measurement of E. M. F.*—The potential measurements were made in a Beckmann apparatus with saturated calomel electrode as the reference. This was directly dipped into the solution under examination, with the platinum electrode also immersed in the same solution. The apparatus was first adjusted by measuring the  $p_{\text{H}}$  of a buffer solution. The solution of each of the cobaltic complexes was prepared as follows: 100 c.c. of a solution containing cobaltous chloride and hydrochloric acid in different proportions were prepared. A weighed amount of the complex salt was taken and dissolved in a 50 c.c. volumetric flask by means of the above mentioned acid cobaltous chloride solution added up to the mark. This was kept at the room temperature for about three days. On the fourth day, when the system had attained equilibrium, measurements were taken. The platinum electrode was kept immersed in a portion of the solution in a test tube some hours before measurement for rapid attainment of equilibrium during the experiments. To begin with, the  $p_{\text{H}}$  of the acid cobaltous solution was measured using calomel and glass electrodes. Then the  $p_{\text{H}}$  of the complex solution was determined. Finally, the glass electrode was replaced by the platinum electrode and the potential developed was measured. The results of the experiments are arranged in Tables III—IX.

The curves obtained by plotting  $\bar{n}$  against  $p_{[b]}$  for solutions of the complexes are also given, where

$$\bar{n} = \frac{3C-x}{C} \text{ and } p_{[b]} = p \frac{[\text{BigH}_2^+]}{[\text{H}^+]}$$

FIG 1

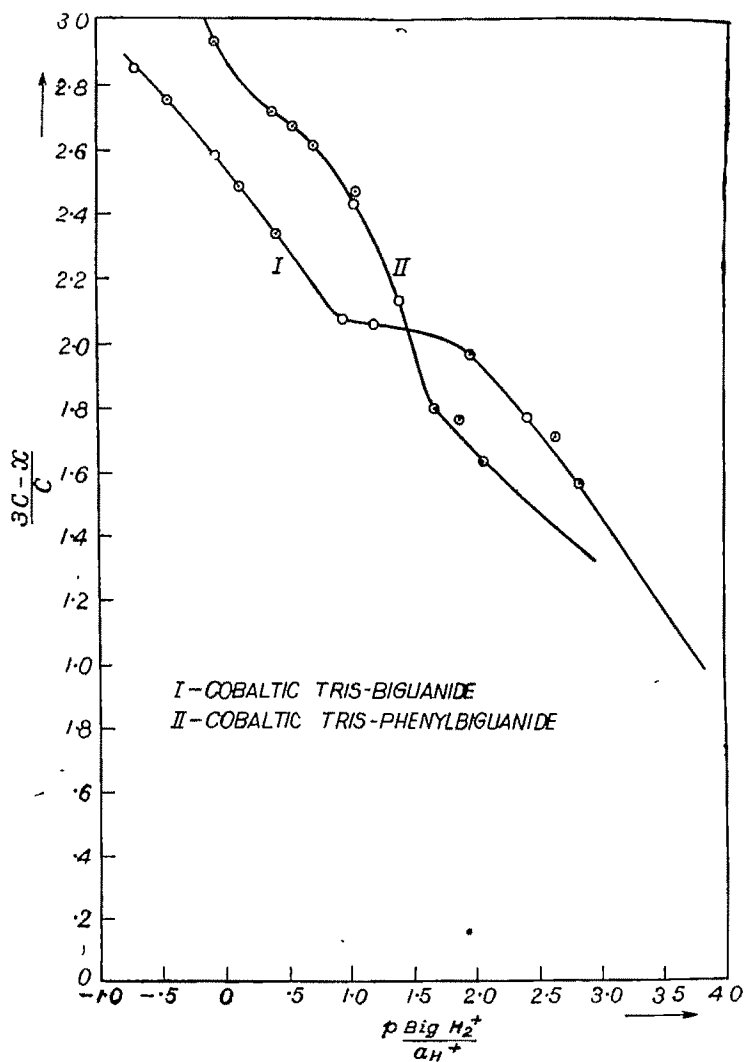


TABLE I

Acid dissociation constant of biguanide,  $k^*_2$

Used  $\text{BigH} \cdot \text{HCl} - 0.01M$  solution  $= C_b$ ;  $C_A$  = total acid = acid added + acid as  $\text{HCl}$  in  $\text{BigH} \cdot \text{HCl}$ .  $C'_A$  = acid corresponding to measured  $p_H$  (from the  $p_H - C_H$  graph).

$C_A$	$p_H$	$C'_A \times 10^3$	$k^*_2 \times 10^3$	$k^*_1$
0.012M	3.62	0.2661	1.144	$3.02 \times 10^{-12}$ (from Das Sarma's data, loc. cit.)
0.013	3.40	0.4508	1.164	
0.014	3.23	0.6730	1.181	
0.016	2.99	1.1590	1.089	
$k^*_2$ (mean) $= 1.15 \times 10^{-3}$				

TABLE II

*Acid dissociation constant of phenylbiguanide ( $k^*_2$ )*Used PhBigH.HCl = 0.01M solution =  $C_A$ .

$C_A$	$p_H$	$C'_A \times 10^3$	$k^*_2 \times 10^3$	$k^*_1$
0.014M	2.77	1.995	6.770	$1.9 \times 10^{-11}$
0.016	2.55	3.311	7.660	(from Das Sarma's
0.018	2.41	4.853	8.480	(data)

 $k^*_2$  (mean) =  $7.27 \times 10^{-3}$ 

TABLE III

*Cobaltic tris-biguanide chloride—acid variation.*

$t = 33^\circ$ . Complex = 0.02M.  $Co^{++} = 0.004M$ .  $k^*_2 = 1.15 \times 10^{-3}$ .  $E_0 = 1.8305$  volt at  $33^\circ$ .  $C_A$  = acid added.  $C'_A$  = acid corresponding to the measured  $p_H$ .  $x$  = total biguanide liberated from the complex.

$C_A$ (corrected)	E.M.F. (in volts)	$p_H$	$C'_A \times 10^3$	$x \times 10^3$	$[BigH_2^+] \times 10^3$	$k'_3$	$k'_2$	$k'_1$	$K'$	$p \frac{[BigH_2^+]}{a_{H^+}}$	$\frac{3C-x}{C} = \bar{n}$
0.004M	0.7029	3.37	0.483	2.770	2.0200	0.7617	...	...	$65.5 \times 10^{-19}$	-0.6755	2.8615
0.008	0.7369	3.00	1.156	4.672	2.5000	0.7615	...	...	$39.21 \times 10^{-19}$	-0.3978	2.7764
0.016	0.7439	2.62	2.818	7.963	2.5480	0.7028	...	...	$4.99 \times 10^{-19}$	-0.0262	2.6018
0.050	0.7719	1.88	16.000	17.710	1.4200	0.8300	...	...	$0.08 \times 10^{-19}$	2.9676	2.1145
0.100	0.8849	1.34	60.810	19.850	0.4870	1.4100	...	...	$0.08 \times 10^{-19}$	1.9725	2.0075
0.160	0.9639	1.06	112.700	23.800	0.3101	...	$8.4 \times 10^{-4}$	$1.08 \times 10^{-17}$	...	2.4484	1.8100
0.200	0.9909	0.94	150.700	24.750	0.2456	...	$7.2 \times 10^{-4}$	$2.65 \times 10^{-17}$	...	2.6697	1.7600
0.250	1.0249	0.83	195.000	27.620	0.2128	...	$8.8 \times 10^{-4}$	$3.86 \times 10^{-17}$	...	2.8620	1.6190

 $k'_3$  (mean) = 0.765 (omitting the borderline doubtful value, 1.410) $k'_2$  (mean) =  $8.13 \times 10^{-4}$  $k'_1$  (mean) =  $2.83 \times 10^{-17}$  $K'$  (mean) =  $k'_1 \cdot k'_2 \cdot k'_3 = 0.176 \times 10^{-19}$ 

From curve I of the graph,

$$Y_2 = 0.11 \times 10^4; k'_2 = \frac{1}{0.11 \times 10^4} = 9.09 \times 10^{-4}.$$

$$Y_3 = 0.16 \times 10; k'_3 = \frac{1}{0.16 \times 10} = 0.625.$$

TABLE IV

*Cobaltic tris-biguanide chloride— $Co^{++}$  variation.*

$t = 33^\circ$ . Complex = 0.02M. Acid = 0.016M.  $k^*_2 = 1.15 \times 10^{-3}$ .  $E_0 = 1.8305$  volt.

$Co^{++}$	E.M.F. (corr.)	$p_H$	$C'_A \times 10^3$	$x \times 10^3$	$[BigH_2^+] \times 10^3$	$k'_3$	$k'_2$	$k'_1$	$K'$	$p \frac{[BigH_2^+]}{a_{H^+}}$	$\frac{3C-x}{C} = \bar{n}$
0.002M	0.7459	2.64	2.685	7.998	2.674	0.7776	...	...	$3.59 \times 10^{-19}$	-0.0672	2.600
0.004	0.7439	2.62	2.818	7.963	2.548	0.7028	...	...	$4.99 \times 10^{-19}$	-0.0262	2.602
0.008	0.7449	2.62	2.818	7.963	2.548	0.7028	...	...	$5.00 \times 10^{-19}$	-0.0262	2.602
0.016	0.7499	2.60	2.972	7.727	2.427	0.6080	...	...	$1.14 \times 10^{-19}$	0.0150	2.614

 $k'_3$  (mean) = 0.698

TABLE V

*Cobaltic tris-biguanide chloride—complex variation.*Co<sup>++</sup> = 0.004M. Acid = 0.016M. *t* = 33°. *E*<sub>0</sub> = 1.8305 volt. *k*<sub>2</sub><sup>\*</sup> = 1.15 × 10<sup>-8</sup>.

Complex.	E.M.F. (corr.)	<i>p</i> <sub>H</sub>	<i>C</i> <sub>A</sub> × 10 <sup>3</sup>	<i>x</i> × 10 <sup>3</sup>	[BigH <sub>2</sub> <sup>+</sup> ] × 10 <sup>3</sup>	<i>k</i> <sub>3</sub>	<i>k</i> <sub>2</sub>	<i>k</i> <sub>1</sub>	<i>K</i> <sub>3</sub>	<i>p</i> $\frac{[\text{BigH}_2^+]}{a_{H^+}}$	$\frac{3C-x}{C} = \bar{n}$
0.02 M	0.7439	2.62	2.818	7.963	2.548	0.7028	...	..	4.99 × 10 <sup>-19</sup>	-0.0261	2.6012
0.015	0.7499	2.52	3.556	7.210	1.990	0.6099	...	..	2.32 × 10 <sup>-19</sup>	0.1812	2.5186
0.010	0.7559	2.39	4.864	6.250	1.377	0.5635	...	..	0.82 × 10 <sup>-19</sup>	0.47.2	2.375c
0.004	0.7479	2.11	9.333	3.587	0.463	0.5181	...	...	0.03 × 10 <sup>-19</sup>	1.2246	2.1000

*k*<sub>3</sub> (mean) = 0.599.

TABLE VI

*Cobaltic tris-phenylbiguanide chloride*—[Co(PhBigH)<sub>3</sub>] Cl<sub>3</sub>, 2.5H<sub>2</sub>O.

Acid variation.

*t* = 33°. Complex = 0.02M. Co<sup>++</sup> = 0.004M. *k*<sub>2</sub><sup>\*</sup> = 7.27 × 10<sup>-8</sup>. *E*<sub>0</sub> = 1.8305 volt.

<i>C</i> <sub>A</sub>	E.M.F. (corr.)	<i>p</i> <sub>H</sub>	<i>C</i> <sub>A</sub> × 10 <sup>3</sup>	<i>x</i> × 10 <sup>3</sup>	[BigH <sub>2</sub> <sup>+</sup> ] × 10 <sup>3</sup>	<i>k</i> <sub>3</sub>	<i>k</i> <sub>2</sub>	<i>k</i> <sub>1</sub>	<i>K</i> <sub>3</sub>	<i>p</i> $\frac{[\text{BigH}_2^+]}{a_{H^+}}$	$\frac{3C-x}{C} = \bar{n}$
0.004M	0.6969	2.82	1.750	1.921	1.590	0.1116	—	—	54.30 × 10 <sup>-21</sup>	-0.0213	2.9540
0.008	0.7009	2.50	3.750	3.262	2.274	0.1402	—	—	22.20 × 10 <sup>-21</sup>	0.1433	2.8370
0.016	0.7219	2.16	8.318	5.166	2.646	0.1332	—	—	8.26 × 10 <sup>-21</sup>	0.4173	2.7420
0.050	0.7409	1.60	31.190	10.590	2.378	0.1065	—	—	0.78 × 10 <sup>-21</sup>	1.0239	2.4700
0.100	0.7819	1.27	68.870	16.540	1.972	0.1754	—	—	0.30 × 10 <sup>-21</sup>	1.4352	2.1730
0.160	0.8059	1.05	115.900	22.970	1.728	—	33.7 × 10 <sup>-4</sup>	3.45 × 10 <sup>-19</sup>	—	1.7124	1.8515
0.200	0.8259	0.93	154.200	23.590	1.374	—	25.6 × 10 <sup>-4</sup>	3.35 × 10 <sup>-19</sup>	—	1.9319	1.8230
0.250	0.8379	0.82	199.500	25.760	1.180	—	31.5 × 10 <sup>-4</sup>	2.41 × 10 <sup>-19</sup>	—	2.1081	1.7120

*k*<sub>3</sub> (mean) = 0.123 (omitting the borderline value, 0.1754)*k*<sub>2</sub> (mean) = 30.30 × 10<sup>-4</sup>*k*<sub>1</sub> (mean) = 3.07 × 10<sup>-19</sup>*K*<sub>3</sub> (mean) = *k*<sub>1</sub>.*k*<sub>2</sub>.*k*<sub>3</sub> = 0.114 × 10<sup>-22</sup>

From curve II of the graph,

*Y*<sub>2</sub> = 0.044 × 10<sup>4</sup>, *k*<sub>2</sub> = 1/*Y*<sub>2</sub> = 22.7 × 10<sup>-4</sup>*Y*<sub>3</sub> = 10.10, *k*<sub>3</sub> = 1/*Y*<sub>3</sub> = 0.099.

TABLE VII

*Cobaltic tris-phenylbiguanide chloride*—Co<sup>++</sup> variation.Complex = 0.02M. *C*<sub>A</sub> = 0.016M.

Co <sup>++</sup>	E.M.F. (corr.)	<i>p</i> <sub>H</sub>	<i>C</i> <sub>A</sub> × 10 <sup>3</sup>	<i>x</i> × 10 <sup>3</sup>	[BigH <sub>2</sub> <sup>+</sup> ] × 10 <sup>3</sup>	<i>k</i> <sub>3</sub>	<i>k</i> <sub>2</sub>	<i>k</i> <sub>1</sub>	<i>K</i> <sub>3</sub>	<i>p</i> $\frac{[\text{BigH}_2^+]}{a_{H^+}}$	$\frac{3C-x}{C} = \bar{n}$
0.002M	0.7179	2.17	8.128	5.311	2.752	0.1471	—	—	4.36 × 10 <sup>-21</sup>	0.3904	2.7340
0.004	0.7219	2.16	8.318	5.166	2.646	0.1332	—	—	8.26 × 10 <sup>-21</sup>	0.4173	2.7420
0.008	0.7099	2.15	8.511	5.014	2.540	0.1199	—	—	7.39 × 10 <sup>-21</sup>	0.4451	2.7490
0.016	0.7049	2.13	8.913	4.710	2.332	0.0969	—	—	2.33 × 10 <sup>-21</sup>	0.5022	2.7640

*k*<sub>3</sub> (mean) = 0.124.



TABLE VIII

*Cobaltic tris-phenylbiguanide chloride—complex variation.*

$$\text{Co}^{++} = 0.004M. \quad C_A = 0.016M.$$

Complex.	P.M.F. (corr.).	$\bar{p}_H$ .	$C_A \times 10^3$ .	$x \times 10^3$ .	$[\text{BigH}_2^+]$ $\times 10^3$ .	$k'_3$ .	$k'_2$ .	$k'_1$ .	$K'$ .	$p \frac{[\text{BigH}_2^+]}{a_H^+}$ .	$\frac{\bar{C}-x}{C} = n$ .
0.020 <i>M</i>	0.7219	2.16	8.318	5.166	2.646	0.1332	—	—	$8.26 \times 10^{-21}$	0.4173	2.7420
0.015	0.7499	2.11	9.333	4.398	2.127	0.1137	—	—	$12.25 \times 10^{-21}$	0.5622	2.7113
0.010	0.7389	2.06	10.520	3.546	1.674	0.1019	—	—	$4.09 \times 10^{-21}$	0.7324	2.6450
0.004	0.7249	2.02	11.480	1.941	0.815	0.0804	—	—	$0.67 \times 10^{-21}$	1.0590	2.5150

$$k'_3 \text{ (mean)} = 0.1073.$$

TABLE IX

*Instability constants.*

$$k_3 = k'_3 \cdot k_1^* ; k_2 = k'_2 \cdot k_1^* ; k_1 = k'_1 \cdot k_1^* ; K = K' \cdot k_1^{*3} = k_1 \cdot k_2 \cdot k_3.$$

	Cobaltic <i>tris</i> -biguanide.	Cobaltic <i>tris</i> -phenylbiguanide.
Acid variation		
$k_3$	$0.765 \times 3.02 \times 10^{-12} = 2.31 \times 10^{-12}$	$0.123 \times 1.9 \times 10^{-11} = 2.34 \times 10^{-12}$
$k_2$	$8.13 \times 10^{-4} \times 3.02 \times 10^{-12} = 2.46 \times 10^{-15}$	$30.3 \times 10^{-4} \times 1.9 \times 10^{-11} = 5.76 \times 10^{-14}$
$k_1$	$2.83 \times 10^{-17} \times 3.02 \times 10^{-12} = 8.55 \times 10^{-29}$	$3.07 \times 10^{-19} \times 1.9 \times 10^{-11} = 5.8 \times 10^{-30}$
$K$ (from direct measurement of $K'$ )	$(1805 \pm 2.26) \times 10^{-55}$	$(370 \pm 2.06) \times 10^{-64}$
$K = k_1 \cdot k_2 \cdot k_3$	$4.85 \times 10^{-55}$	$0.78 \times 10^{-64}$
Co <sup>++</sup> variation		
$k_3$	$0.698 \times 3.02 \times 10^{-12} = 2.11 \times 10^{-12}$	$0.1243 \times 1.9 \times 10^{-11} = 2.36 \times 10^{-12}$
$K$ (from direct measurement of $K'$ ).	$(137.5 \pm 31.3) \times 10^{-55}$	$(57 \pm 16) \times 10^{-64}$
Complex variation		
$k_3$	$0.599 \times 3.02 \times 10^{-12} = 1.81 \times 10^{-12}$	$0.1078 \times 1.9 \times 10^{-11} = 2.04 \times 10^{-12}$
$K$ (from direct measurement of $K'$ )	$(137.5 \pm 0.83) \times 10^{-55}$	$(84 \pm 4.6) \times 10^{-64}$
Graphical values (from the curves).		
$k_3$	$0.625 \times 3.02 \times 10^{-12} = 1.89 \times 10^{-12}$	$0.099 \times 1.9 \times 10^{-11} = 1.88 \times 10^{-12}$
$k_2$	$9.09 \times 10^{-4} \times 3.02 \times 10^{-12} = 2.75 \times 10^{-15}$	$22.5 \times 10^{-4} \times 1.9 \times 10^{-11} = 4.275 \times 10^{-14}$

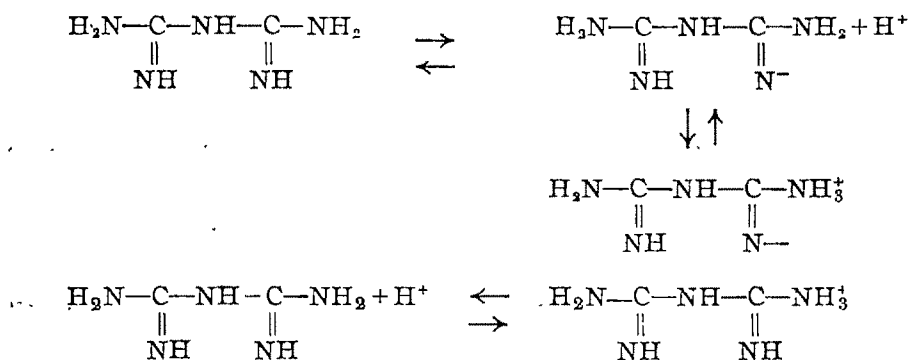
## DISCUSSION

From a consideration of Table I and Table II it will be observed that the acid dissociation constant of simple biguanide is smaller than that of phenylbiguanide; hence the simple biguanide, as is to be expected, behaves as a somewhat stronger base than its phenyl analogue.

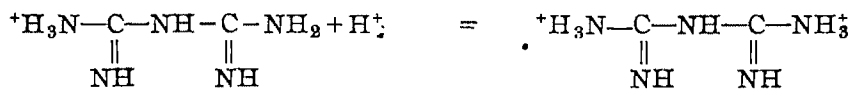
A comparison of the acid dissociation constant values of the simple and phenylbiguanides with those of ammonia, aliphatic and aromatic amines, as given below, shows that as a mono-acid base, they are as strong as dialkyl and monoalkyl amines.

Amine.	$K_{AH}^+$	$K_{AB_2}^{++}$	
$CH_3NH_2$	$2.8 \times 10^{-11}$	..	{ From Britton & Williams values of $K_b$ ( <i>J. Chem. Soc.</i> , 1935, 796).
$C_2H_5NH_2$	$2.5 \times 10^{-11}$	...	
$(CH_3)_2NH$	$1.1 \times 10^{-11}$	..	
$(C_2H_5)_2NH$	$5.9 \times 10^{-12}$	...	
$(CH_3)_3N$	$1.6 \times 10^{-10}$	...	{ From Earned and Owens values of $K_b$ , ( <i>J. Amer. Chem.</i> <i>Soc.</i> , 1930, 82, 5090).
$(C_2H_5)_3N$	$1.5 \times 10^{-11}$	...	
$C_6H_5NH_2$	$3.7 \times 10^{-10}$	..	
$NH_3$	$5.6 \times 10^{-10}$	...	
$C_2H_4(NH_2)_2$	$1.2 \times 10^{-10}$	$6.4 \times 10^{-8}$	{ Carlson, Mc Reynolds & Verhoek, <i>ibid.</i> , 1945, 67, 1336.
$C_3H_6(NH_2)_2$	$1.48 \times 10^{-10}$	$8.5 \times 10^{-8}$	
$C_2N_5H_7$	$3.02 \times 10^{-12}$	$1.15 \times 10^{-3}$	
Biguanide.			
$C_6H_5C_2N_5H_6$	$1.9 \times 10^{-11}$	$7.27 \times 10^{-3}$	
Phenylbiguanide.			

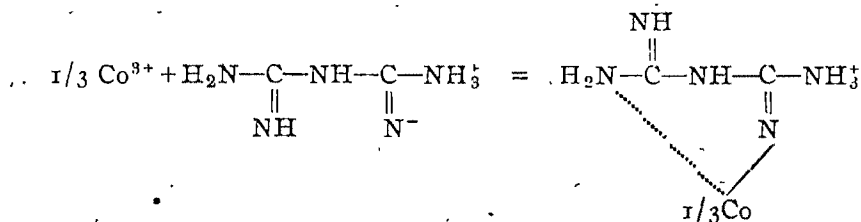
But the second dissociation constant  $K_{AB_2}^{++}$  are, on the other hand, considerably larger, being of the order of  $10^{-3}$  as against  $10^{-8}$  of the alkyl diamines and  $10^{-5}$  of aniline. This can reasonably be attributed to the ampholytic character of biguanides which enables them to give rise to inner metallic complexes in combination with metallic ions of transitional elements. Thus, we may write :



As the second acid dissociation constant of biguanide is quite large, we may ignore the formation of ions of the type :



and consider the biguanides as mono-acidic base, but capable of behaving to a small extent as an ampholyte in solution giving zwitter or dipolar ions as indicated before, responsible for the formation of inner metallic complexes with suitable metal ions. Thus



It has been observed that phenylbiguanide is somewhat weaker base than the simple biguanide. It will also be found from Table IX, in which the average values of instability constants for the successive partial stages, as well as for the overall stage, of the cobaltic complex with these two ligands under different conditions have been collected side by side for convenience of comparison, that phenylbiguanide, on the whole, gives rise to somewhat less stable complex than the simple biguanide. The table also shows that the overall instability constant  $K$ , determined from the direct measurement of  $K'$ , varies rather widely in each case and under any specified condition. This might evidently be attributed to the fact that the values of  $K'$  is based on the determination of cobaltic ion concentration by means of E.M.F. measurements, which required the use of  $E_0$  of cobaltic-cobaltous system. This value was taken from Lamb and Larson's work (*loc. cit.*) after necessary temperature correction. These authors in their measurement employed strongly acid (8N) solutions, while our measurements were all made in solutions not exceeding 0.25 N in acid strength. There is likelihood that the value of  $E_0$  for the cobaltic-cobaltous system might vary with the acid concentration of the solution leading to a variation in the overall  $K$  value. This variation might as well be caused by the fact that the cobaltic ion concentration in weakly acid solutions of the complex is negligibly small, and the slight error in its measurement is bound to give rise to widely different values. The instability of the cobaltic ion itself in solution also obviously plays an important part in causing this variation. On the other hand, the value of  $K$  can more satisfactorily be deduced from the product of the instability constants  $k_1$ ,  $k_2$ , and  $k_3$  for the successive partial complexes. The value of  $k_1$ , which is also based on cobaltic ion concentration, determined from E.M.F. measurement, was found to remain fairly constant as it was measured in fairly strong acid solutions (0.16-0.25M), where an appreciable amount of cobaltic ion is likely to prevail. The values of  $k_3$  and  $k_2$  for both simple and phenylbiguanide complexes were also calculated from the equation derived by following the method of Carlson and co-workers (*loc. cit.*) with the help of the curves obtained by plotting  $(3C-x)/C$  against  $p$  ( $[BiH_2^+]/a_H^+$ ). It will be found from Table IX that these agree more or less closely with the experimental values, proving thereby the validity of Carlson and co-workers' method.

The results obtained justify the assumption that the *tris*-biguanide complexes dissociate and decompose in three successive stages as already discussed. The instability constants  $k_3$ ,  $k_2$  and  $k_1$  for the successive *tris*-, *bis*- and mono-biguanide complexes, as shown in Table IX, progressively decrease, as might be expected, with the progressively decreased saturation of the co-ordinating affinity of the central cobaltic ion by the biguanide ligands. The overall instability constants ( $K=4.85 \times 10^{-55}$  for the simple biguanide complex and  $7.8 \times 10^{-55}$  for the phenylbiguanide complex) are quite low; that for cobaltic hexammine, as determined by Lamb and Larson (*loc. cit.*), is of the order of  $10^{-34}$ . This is in keeping with the expectation that biguanide complexes, being of the inner metallic type, should show a greater stability than the co-ordination complexes of the usual hexammine type.

The overall instability constants for the simple and phenylbiguanide complexes may now be compared to those of inner metallic complexes of salicylaldehyde and

acetylacetone with copper, as determined by Calvin and Wilson (*J. Amer. Chem. Soc.*, 1945, **67**, 2905).

Complex.	$k_1$ .	$k_2$ .	$k_3$	$K$ .	$K_{1n}^+$
Cu <sup>II</sup> -salicylaldehyde	$3.2 \times 10^{-8}$	$1.6 \times 10^{-8}$	..	$5.12 \times 10^{-14}$	$3.2 \times 10^{-10}$
Cu <sup>II</sup> -acetylacetone	$1.0 \times 10^{-9}$	$8.0 \times 10^{-9}$	..	$8.00 \times 10^{-13}$	$2.0 \times 10^{-10}$
Co <sup>III</sup> -biguanide	$8.55 \times 10^{-29}$	$2.46 \times 10^{-15}$	$2.28 \times 10^{-12}$	$4.35 \times 10^{-55}$	$3.02 \times 10^{-12}$
Co <sup>III</sup> -phenylbiguanide	$5.8 \times 10^{-30}$	$5.76 \times 10^{-14}$	$2.34 \times 10^{-12}$	$7.8 \times 10^{-56}$	$1.9 \times 10^{-11}$

In the case of cobaltic biguanide complexes the  $k_1$  and  $k_2$  values are exceedingly smaller than those of copper salicylaldehyde and copper acetylacetone, and the  $K_{1n}^+$  values too are somewhat smaller. Hence, the nature and valency of the central ion, as also the nature of the ligand, obviously exert a considerable influence on the stability of the complex, particularly when the ligands are of polar character, as in the present cases. The higher valency of the cobaltic ion undoubtedly increases the stability of its complexes.

Instability constants for complexes of many neutral ligands like ammonia, ethylenediamine, etc., with bivalent metals, namely Cu, Ni, Co, Zn, and Cd, have been determined by Carlson and co-workers (*loc. cit.*), as well as by Bjerrum (*loc. cit.*). These (overall  $K$  values) generally lie between  $10^{-20}$  and  $10^{-6}$  depending upon the nature of the metal and the character of the ligand. The cobaltic biguanide complexes therefore present instances of the most stable cationic co-ordination complexes hitherto examined.

INORGANIC CHEMISTRY LABORATORY,  
UNIVERSITY COLLEGE OF SCIENCE  
AND TECHNOLOGY, CALCUTTA.

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## KINETIC STUDY OF THERMAL DECOMPOSITION OF TIN AND SILICON TETRAMETHYLS

BY T. V. SATHYAMURTHY, S. SWAMINATHAN AND LOURDU M. YEDDANAPALLI

The experimental results of Waring and Horton on the thermal decomposition of tin tetramethyl have been re-examined and shown to fit in better with a three-halves order rate constant and a free radical kinetic mechanism than with a unimolecular rate constant and a molecular rearrangement mechanism put forward by the authors. Also, the results of Helm and Mack on the thermal decomposition of silicon tetramethyl in the low pressure region, not amenable to first or second order kinetic expressions, have satisfactorily been interpreted in terms of three-halves order reaction involving a free radical mechanism.

With the classical work of Paneth and Hofeditz (*Ber.*, 1929, **62**, 1335) demonstrating the presence of free radicals in the thermal decomposition of lead tetramethyl, and the illustration of the wide applicability of free radical mechanism to the kinetics of vapour phase thermal decomposition of both metal alkyls and many organic compounds (Rice and Rice, "The Aliphatic Free Radicals", 1935), attempt has been made to account even for the kinetics of the so-called quasi-unimolecular reactions in terms of atomic and free radical mechanism (Rice and Herzfeld, *J. Amer. Chem. Soc.*, 1934, **56**, 284; Pease, "Equilibrium and Kinetics of Gas Reactions", 1942). The recent investigation of the thermal decomposition of aluminium trimethyl (Yeddnapalli and Schubert, *J. Chem. Phys.*, 1946, **14**, 1) revealed the reaction to be kinetically of three-halves order involving a free radical mechanism, the methyl radicals resulting from the primary rupture of Al—C bond of the metal alkyl. Taylor and Cunningham (*ibid.*, 1938, **6**, 357) also assumed the primary process in the thermal decomposition of mercury dimethyl to be the formation of methyl radicals which took part in subsequent reactions leading to the observed products.

In view of these facts, it was rather surprising to find that the thermal decomposition of tin tetramethyl was reported by Waring and Horton (*J. Amer. Chem. Soc.*, 1945, **67**, 540) to be kinetically of first order involving not a free radical but essentially a molecular rearrangement mechanism.\* Another compound which had previously been reported to exhibit a unimolecular thermal decomposition above a certain initial pressure, is silicon tetramethyl (Helm and Mack, *ibid.*, 1937, **59**, 60), although no attempt was made to explain the kinetics of the reaction beyond indicating the possibility of a free radical mechanism. It was thought to be of interest to re-examine the results reported on these metal alkyls from the view point of free radical mechanism.

### *Tin Tetramethyl*

The results of Waring and Horton are presented in Table IA, in which 'r' denotes the fractional decomposition of the metal alkyl initially of a pressure of 100 mm. Hg., and *k*, the calculated unimolecular rate constant. From the rate constants at different temperatures, it was deduced that

$$\log k = 21.92 - (82,400/2.303 RT)$$

where 82,400 cal. per mol. is the activation energy  $E$  of the process. Table Ib contains the recalculated rate constants from the same experimental results on the basis of three-halves order and the corresponding integrated kinetic expression,

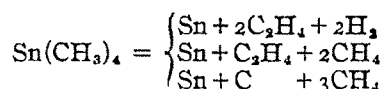
$$k = \frac{2}{t} \left[ \frac{1}{(p_0 - p)^{\frac{1}{2}}} - \frac{1}{p_0^{\frac{1}{2}}} \right]$$

in which  $p$  stands for the pressure at time  $t$  sec. and  $p_0$ , for the initial pressure. The original values of ' $\tau$ ' were transformed, for ease and simplicity of calculation, into pressures in mm. Hg. in keeping with the indicated initial pressure of 100 mm. Hg. On plotting  $\log k$  against  $1/T$ , the slope of the line thus obtained yields for  $E$  a value of 75.9 k cal. per mol. so that the rate constant may be expressed by

$$\log k = 18.92 - (75,900/2.303 RT).$$

Comparison of Tables Ia and Ib brings out the fact that the values of  $k$  for a given temperature are much more constant in the latter than in the former case, due allowance being made for experimental errors. At higher temperatures the comparison tells even more clearly in favour of Table Ib. The recalculated  $E$ , 75.9 k cal. is substantially less than the original value 82.4 k cal., and the corrected frequency factor is about  $10^{19}$ . Though the normal frequency factor for 1.5 order reaction is about  $10^{15}$  (cf. Pease, *loc. cit.*, p. 133), the increased value in the present case may be presumed to be due to an increase in entropy of activation associated with the loose structure of the activated complex as compared with the reactant alkyl molecule.

The supposed unimolecular rate constant was interpreted by Waring and Horton in the sense that the metal alkyl broke down into gaseous products, of which methane formed the major constituent by molecular rearrangement thus,



Although the possibility of rupture of the Sn—C bond to give methyl radicals was recognised, it was, however, accorded only a negligible probability. The rather high value of 82.4 k cal. for  $E$ , was taken as evidence "in favour of a rearrangement mechanism for the decomposition" as against a free radical mechanism. This appears to be contrary to the generally accepted view in reaction kinetics. As Hinshelwood puts it in connection with acetaldehyde decomposition "In the decomposition of a substance such as acetaldehyde, the initial production of a free radical by a process such as  $\text{CH}-\text{CHO} = \text{CH}_2 + \text{CHO}$  will require a higher activation energy than the alternative process of direct molecular rearrangement to  $\text{CH}_4$  and  $\text{CO}$ " (Hinshelwood, "The Kinetics of Chemical Change", 1942, p. 87). Consequently the higher activation energy in the present case would seem to indicate rather a free radical mechanism, without excluding evidently the possibility of a small percentage of molecular rearrangement process also.

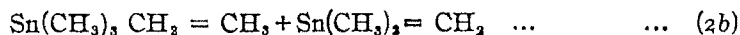
*Proposed Free Radical Mechanism.*—The free radical mechanism in the present case may be represented by the following sequence of reactions:



$\text{Sn}(\text{CH}_3)_3$  may further break down to give more methyl radicals and ultimately metallic tin. The  $\text{CH}_3$  radicals react with metal alkyl to yield methane according to the equation,



The latter radical may, by analogy with other complex radicals, tend to lose a  $\text{CH}_3$  and revert to a stable molecule thus,



This unsaturated product may undergo further reaction or polymerisation, thus accounting for a part of the solid deposit formed on the walls of the reaction vessel. Steps (2a) and (2b) would constitute the reaction chain leading to formation of methane as the major constituent of the gaseous products. The chain breaking process is the recombination of the methyl radicals according to equation,



TABLE IA

 $p_0 = 100 \text{ mm.}$ 

440°.		450°.		467.4°.		484.7°.		493.2°.	
r.	k.10 <sup>3</sup> .	r.	k.10 <sup>3</sup> .	r.	k.10 <sup>3</sup> .	r.	k.10 <sup>3</sup> .	r.	k.10 <sup>3</sup> .
0.1250	0.3151	0.1250	1.191	0.1250	4.268	0.1250	10.86	0.1128	22.34
.1369	.3167	.1354	1.181	.1462	3.681	.1273	16.40	.1250	27.49
.2500	.3311	.2500	1.402	.2500	5.619	.2500	12.51	.2256	24.72
.2738	.3100	.2709	1.305	.2924	5.032	.2546	12.18	.2500	28.54
.4107	.2438	.4063	1.048	.4386	4.729	.3819	11.83	.3384	25.49
.5000	.2021	.5000	0.872	.5000	3.415	.5000	8.84	.4513	21.81
.5476	.1869	.5418	0.645	.5848	3.069	.5092	8.84	.5000	20.41

TABLE IB

 $p_0 = 100 \text{ mm.}$ 

440°.		450°.		467.4°.		484.7°.		493.2°.	
p(mm).	k.10 <sup>4</sup> .	p(mm).	k.10 <sup>3</sup> .	p(mm).	k.10 <sup>3</sup> .	p(mm).	k.10 <sup>-3</sup> .	p(mm).	k.10 <sup>-3</sup> .
87.50	0.3226	87.50	0.1220	87.50	0.4368	87.50	1.1110	88.72	2.297
86.31	.3291	86.46	.1222	85.38	.3825	87.27	1.7000	87.50	2.814
75.00	.3562	75.00	.1509	75.00	.6045	75.00	1.1030	77.44	2.641
72.62	.3367	72.91	.1411	70.76	.5492	74.51	1.3090	75.00	3.068
58.93	.2677	59.37	.1195	56.14	.5489	61.81	1.3420	66.16	2.828
50.00	.2415	50.00	.1042	50.00	.4081	50.00	1.0600	54.87	2.881
45.24	.2217	45.82	.0998	41.52	.3858	49.08	1.6620	50.00	2.439

TABLE II  
Decomposition of silicon tetramethyl.

Initial $p_0 = 149$ mm.					
Time.	Pressure ( $p$ ).	$p_0 - p$ .	$k_1$	$k_2$	$k_{1.5}$
0.00 min.	149.0 mm.				
3.25	266.0	180.0			
4.12	290.5	155.5	0.0028	0.0017	0.0008093
5.33	317.0	129.0	.0026	.0018	.0008333
6.35	334.5	111.5	.0024	.0019	.0008541
7.60	353.0	93.0	.0024	.0023	.0008874
8.78	365.0	81.0	.0020	.0027	.0008917
10.27	378.0	68.0	.0020	.0026	.0009069
11.78	387.5	58.5	.0017	.0026	.0009078
14.33	400.5	45.5	.0015	.0032	.0009230
16.78	408.3	37.7	.0013	.0031	.0009139
19.08	414.5	31.5	.0013	.0038	.0009179
22.43	419.8	26.2	.0009		.0008900
26.42	425.8	20.2	.0011		.0008989
31.10	428.7	17.3	.0006		
97.0	446.0 = $p_0$				

Applying the steady state principle, the concentration of methyl radicals may be calculated in the following manner :

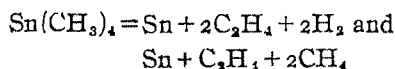
$$\begin{aligned} d[\text{CH}_3]/dt &= k_1[\text{A}] - k_3[\text{CH}_3][\text{CH}_3] = 0 \\ [\text{CH}_3] &= (k_1/k_3)^{1/2}[\text{A}]^{1/2} \end{aligned}$$

in which A denotes the metal alkyl and  $k$ 's the rate constants of the steps indicated by the appropriate subscripts. The overall rate of disappearance of the metal alkyl is given by

$$-d[\text{A}]/dt = k_1[\text{A}] + k_2(k_1/k_3)^{1/2}[\text{A}]^{3/2}.$$

Assuming the initial reaction constant  $k_1$  to be negligible compared to that of the chain process, the overall decomposition rate is seen to be proportional to alkyl concentration raised to three-halves power, in agreement with the revised kinetic order of the reaction (cf. Table Ib).

Step (2a), a radical-molecule reaction, with a relatively small activation energy, 15 k cal. or less, is of rapid occurrence and accounts for the high proportion of methane formed. The small percentages, 5 to 10, of ethylene and hydrogen may be accounted for partly by the dissociation of ethane and partly by the breakdown of the metal alkyl molecules directly according to the equations,



as suggested by Waring and Horton (*loc. cit.*).

The activation energy will be governed essentially by the energy needed to break the Sn—C bond for which no experimental data are at present available and need not be considered further.

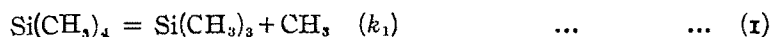


*Silicon Tetramethyl*

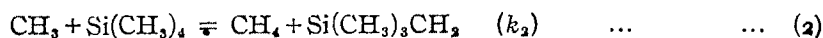
The thermal decomposition of silicon tetramethyl investigated by Helm and Mack (*loc. cit.*) in the temperature range of  $659^{\circ}$ – $717^{\circ}$  was found to be homogeneous and of first order above an initial pressure of 149 mm. Below this, however, the unimolecular character could not be observed, as can be seen from the results in Table II in which column 2 gives pressures  $p$  of the system at various times of reaction, the initial pressure  $p_0$  being 149 mm. Hg., column 3 gives the difference between  $p$  and  $p_{\infty}$  (pressure at complete decomposition) and columns 4 and 5 list the first and second order constants calculated by Helm and Mack, the last column presenting the 1.5 order constants calculated by us according to the integrated kinetic expression given above.

It is evident from Table II that the values of  $k$  in the last column are practically constant within experimental errors over the whole pressure range, whereas those in the two preceding columns do not show such constancy. It is not unreasonable therefore to conclude that the kinetic order of the reaction is three-halves within the indicated pressure range. The products of reaction have been reported to consist mostly of methane (about 60%) and hydrogen (about 40%) with minute amounts of olefines and acetylenes. From the similarity of these products with those obtained from pyrolysis of ethane (Bone and Coward, *J. Chem. Soc.*, 1908, **93**, 1206), the authors suggested the reaction mechanism to be similar in both cases, involving probably methyl radicals as intermediates, without, however, attempting to elaborate such a free radical mechanism. We are therefore tentatively presenting a comprehensive free radical mechanism capable of accounting for the fractional order of reaction at pressures below 149 mm. (cf. Table II) but also for the first order character of the reaction at higher pressures, substantiated in the original paper.

*Proposed Reaction Mechanism.*—The initial step may be considered to be the breaking of one of the Si—C bonds of the alkyl,



the complex radical possibly breaking down to give more methyl radicals and finally Si. The methyl radicals react with alkyl molecules to give methane thus,



The complex radical may be assumed to break down into methyl and ethyl radicals,  $\text{C}_2\text{H}_5 + 2\text{CH}_3 + \text{Si}$ , the  $\text{C}_2\text{H}_5$  undergoing further decomposition,



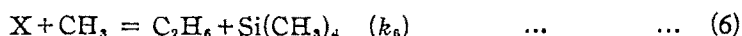
and the H atoms reacting with alkyl molecules yielding the next major product after methane, namely, gaseous hydrogen according to the equation,



This complex radical will undergo the change already indicated. At higher alkyl pressures, there is the possibility of an adduct between methyl radicals and alkyl molecules of the type indicated below, justification for which may be found in the recent paper of Noyes, Jr. and Gomer (*J. Amer. Chem. Soc.*, 1949, **71**, 3390),



where X stands for the complex adduct which may then react with a methyl radical according to the equation,



these two steps forming the chain ending processes at higher alkyl pressures. At lower alkyl pressures, the methyl radicals may interact mutually to give ethane,



Now to account for 1.5 order below 149 mm. pressure of alkyl, steps 1 to 4 and 7 are to be taken for the reasons just given. Applying the steady state principle and representing the alkyl by A, the concentrations of the appropriate active species are found to be expressed by,

$$[CH_3] = (k_1/k_7)^{\frac{1}{2}}[A]^{\frac{1}{2}} \text{ and } [H] = (k_2/k_4)(k_1/k_7)^{\frac{1}{2}}[A]^{\frac{1}{2}}.$$

The overall rate of decomposition of the alkyl is given by,

$$-d[A]/dt = k_1[A] + k_2[CH_3][A] + k_4[H][A]$$

which on substituting for the active species, becomes

$$-d[A]/dt = k_1[A] + 2k_2(k_1/k_7)^{\frac{1}{2}}[A]^{\frac{3}{2}}.$$

Neglecting the slow initial reaction in comparison with the chain reaction steps, the overall rate is seen to be proportional to the concentration of the alkyl raised to power 1.5 in agreement with the recalculated order for the results given in Table II.

At initial pressures higher than 149 mm. Hg., the sequence of reaction steps to be taken into account, for reasons already adduced, are 1 to 6 inclusively. Calculations similar to the ones given above lead, for the overall rate of disappearance of alkyl, to the expression,

$$-d[A]/dt = k_1[A] + 2k_1k_2/(k_2 + 2k_8) \cdot [A].$$

Neglecting as before  $k_1$  for reasons already given, the overall rate of decomposition of the alkyl is proportional to its simple concentration, and the reaction is therefore of first order, as actually observed by Helm and Mack (*loc. cit.*).

The above mechanism accounts for the reaction products being mainly methane and hydrogen, the ethane formed by the chain breaking steps, small in amount, being decomposed at the high temperature of the reaction. Nothing definite can be said about the activation energy of the three-halves order reaction since data are available only at one temperature. As a part of a comprehensive programme of research on the decomposition of metal alkyls, it is proposed to make a thorough investigation of the above two alkyls in order to be able to secure a more complete picture of their reaction kinetics.

## INTERACTION OF NITROUS ACID AND METHYLAMINE: INFLUENCE OF THE ACIDITY OF THE MEDIUM

By R. H. SAHASRABUDHEY

Increasing acidity initially favours the amine-nitrous acid reaction; subsequently a critical point is reached any increase beyond which suppresses the reaction. The self decomposition of nitrous acid, which more or less, always accompanies this change, also shows a similar initial augmentation, followed in this case by attainment of a maximum rate of decomposition. Comparison of the results with those obtained with ammonium chloride and thiocarbamide suggests that the mechanism of  $-\text{NH}_2-\text{HNO}_2$  interaction is similar in all the three cases.

When nitrous acid interacts with carbamide (Werner, *J. Chem. Soc.*, 1917, 111, 863), thiocarbamide (Werner, *ibid.*, 1912, 101, 2180; Coade and Werner, *ibid.*, 1913, 103, 1221) and amides (Plimmer, *ibid.*, 1925, 2651; Sidgwick, Taylor and Baker, "The Organic Chemistry of Nitrogen", Oxford, 1942, reprint, pp. 23, 349), the acidity of the medium is a factor of prime importance. Little information, save the observations of Taylor (*J. Chem. Soc.*, 1928, 1099, 1897), is, however, available on the influence of this factor on the amine-nitrous acid reaction. The present investigation was therefore undertaken to extend these studies to a simple-amine, like methylamine.

### EXPERIMENTAL

The experiments were carried out with methylamine hydrochloride prepared by the methylation of ammonium chloride by formaldehyde (Werner, *J. Chem. Soc.*, 1917, 111, 844).

It was purified from dimethylamine and ammonium chloride by repeated crystallisation from alcohol and treatment with dry chloroform. The purity of the sample was confirmed by estimating the amine. A normal solution of this was used as the stock solution. As a source of nitrous acid, normal sodium nitrite solution, standardised by the thiourea method (cf. Coade and Werner, *loc. cit.*), was used.

Experiments were carried out in a Lunge's nitrometer using mg. molar quantities of the reactants. The reaction medium was the acid of the desired concentration. After mixing the reactants by gently shaking the nitrometer, the reaction was allowed to proceed for a fixed duration of time at the end of which the gas was measured and its composition determined (Werner, *loc. cit.*).

Attempts were made earlier to measure the velocity of this interaction by observing the rate of gas evolution (Arndt, *Z. physikal. Chem.*, 1901, 39, 64: 1903, 45, 570; Blanchard, *ibid.*, 1902, 41, 681; Euler, *Annalen*, 1903, 330, 280), but since nitric oxide formed by the decomposition of  $\text{HNO}_2$  was invariably present and in certain cases (*vide infra*) formed the bulk of the evolved gas, these observations did not always give a correct picture of the amine-nitrous acid interaction. As, in the present case, known quantities of both the reactants have been used and the gaseous products also have been measured and analysed, the observations, it is felt, represent a reasonably

correct picture of the change. Other objections (Taylor, *J. Chem. Soc.*, 1928, 1099) to the procedure followed might be : (i) that unless the reactants are continuously and thoroughly agitated the rate of gas evolution cannot be an accurate measure of the velocity of the reaction, and (ii) such agitation greatly increases the rate of decomposition of nitrous acid. A third possible objection is the presence of solid particles (*e.g.* those of barium sulphate in Taylor's experiments) which also greatly increase the decomposition of nitrous acid.

As will be evident from the results shown in Table I, a comparison of the composition of the gas evolved (approximately at constant volume), when the nitrometer is vigorously shaken during the reaction time and when it is kept undisturbed after mixing the reactants, leaves little doubt that the reaction under both conditions follows substantially the same course, except that in the former case it is accelerated as a whole due to shaking. There is no evidence of a specially increased rate of nitrous acid decomposition.

TABLE I

Reaction mixture shaken during the expt				Reaction mixture undisturbed during the expt.					
Duration of experiments									
Medium	Total gas (c.c.)*	15 mins.		Total gas (c.c.)	60 mins.		Total gas.	24 hours	
		% N <sub>2</sub> .	% NO.		% N <sub>2</sub> .	% NO.		% N <sub>2</sub>	% NO.
Acetic acid 6%	...	...	...	...	...	..	16.0	75.5	24.5
10	...	...	..	7.3	71.2	28.8	19.0	74.7	25.3
20	8.3	85.5	14.5	9.0	72.2	27.8	19.3	65.3	34.7
40	10.3	64.0	36.0	10.5	66.6	33.4	19.8	61.1	38.9
66	9.8	32.9	67.1	8.8	35.2	64.8	16.4	50.0	50.0
2N-H <sub>2</sub> SO <sub>4</sub>	9.8	5.1	94.9	6.2	2.0	98.0	11.9	3.0	97.0

In the present experiments, there were no solid particles in the medium except in the case of reactions in sulphuric acid, where due to the action of nitrous acid on mercury a black powdery deposit (presumably, an oxide of mercury) was formed during the reaction. Under a uniform procedure of experimentation therefore the results are quite comparable.

The results with methylamine have been presented in Tables II-IV and in Figs. 1 and 2. Experiments were also carried out with ammonium chloride (Merck's A. R.) and thiocarbamide following similar procedure. A comparison of the typical results with methylamine and these substances has been shown in Table V and graphically in Fig. 3.

\* These volumes are directly comparable because all the experiments were carried out between 22° and 25° and 758 and 759 mm. Hg.

*Estimation of Methylamine*

In experiments 1 and 10 of Table III, and those recorded in Table IV, the residual methylamine was estimated after the fixed period by distillation with NaOH. The method, on previous test, was found to give results accurate to  $\pm 1\%$ .

*Interaction of Nitrous Acid and Methylamine : Influence of the Acid conc. of the Medium and other Factors.*—The experiments were carried out in a Lunge's nitrometer with mg. molar quantities of reactants. Each experiment was allowed to proceed for a duration of one hour, at the end of which the volume of the gas evolved was noted and its composition determined. The progress of the reaction was followed by observing the volume of the evolved gas every ten minutes. By adopting a uniform procedure the results, on repeating the experiments, showed agreement within 5% (Table II).

TABLE II

Expt. No.	Reactants.	Medium.	Dilution.	Gas evolved during						Total gas at N.T.P.	Composition of the gas (c.c.)		Remarks.
				10 min. (c.c.)	20 min. (c.c.)	30 min. (c.c.)	40 min. (c.c.)	50 min. (c.c.)	60 min. (c.c.)		%N.	%NO.	
1	Me NH <sub>2</sub> .HCl and HNO <sub>2</sub> in 1:1 ratio	6% Acetic acid.	5 c.c.	0.9	1.3	2.6	3.6	4.2	4.9		7	8	9
2	"	10%	"	1.8	3.4	4.7	5.7	6.5	7.3	6.45 c.c.	71.2 (5.2)	28.8 (2.1)	
3	2:1	"	"	2.0	3.8	5.0	6.3	7.5	8.6		87.2 (7.5)	12.8 (1.1)	
4	1:1	"	11	0.4	0.6	0.9	1.2	1.6	1.9				{ Mercury of the nitrometer was covered with CCl <sub>4</sub> .
5	"	"	5	0.5	1.1	1.8	2.6	3.4	4.1				
6	"	20%	"	1.9	4.0	5.9	7.0	8.1	9.0	7.95	72.2 (6.5)	27.8 (2.5)	
7	"	40%	"	3.2	5.0	7.0	8.4	9.5	10.5	9.3	66.6 (7.0)	33.4 (3.5)	
8	HNO <sub>2</sub> only	"	"	2.9	1.4	1.9	2.3	2.7	3.1		0.0 (0.0)	100 (3.1)	
9	As in Expt. 1.	50%	6	4.0	6.2	7.8	8.8	9.6	10.3	9.12	44.6 (4.6)	55.4 (5.7)	
10	"	66%	7.5	3.4	5.0	6.5		8.0	8.8	7.92	35.2 (3.1)	64.8 (5.7)	{ The decrease in the reaction velocity might be due to dilution.
11	"	2N.H <sub>2</sub> SO <sub>4</sub>	5	3.4	3.8	4.5	5.2	5.7	6.2	5.6	2.0 (0.1)	98.0 (6.1)	

(Vide Figs. 1 and 2.)

*Interaction of Nitrous Acid and Methylamine : Influence of Acid conc. and other Factors.*—The experiments were carried out in a Lunge's nitrometer with mg. molar quantities of reactants. Each experiment was allowed to proceed for 24 hours, at the end of which the gas evolved was measured and its composition determined (Table III).

TABLE III

Expt. No.	Reactants.	Medium.	Dilution.	Gas evolved at		Comp. of the gas.		Remarks.
				room temp.	NTP.	%N <sub>2</sub> (c.c.)	%NO (c.c.)	
	2	3	4	5	6	7	8	9
1	Me.NH <sub>2</sub> , HCl and HNO <sub>2</sub> in 1:1 ratio.	6% Acetic acid.	5 c.c.	18.0 c.c.	15.98 c.c.	75.5 (13.6)	24.5 (4.4)	On estimation of methylamine in the reaction mixture (in a separate experiment) 23% were found unused.
2	"	"	"	21.2	—	79.2 (16.8)	20.8 (4.4)	The experiment was allowed 72 hours.
3	"	10% "	"	19.0	16.87	74.7 (14.2)	25.3 (4.8)	
4	"	"	"	17.5	—	83.4 (14.6)	16.6 (2.9)	The mercury was covered by a column of CCl <sub>4</sub> .
5	"	"	11 c.c.	13.6	—	59.4 (8.1)	40.5 (5.5)	
6	"	20% "	5 c.c.	19.3	17.14	65.3 (12.6)	34.7 (6.7)	
7	"	40% "	"	19.8	17.58	61.1 (12.1)	38.9 (7.7)	
8	HNO <sub>2</sub> only	"	"	11.5	—	0.0 (0.0)	100.0 (11.5)	(i) The reaction was allowed only 16 hours.
9	As in Expt. 1	66% "	"	16.4	14.56	50.0 (8.2)	50.0 (8.2)	(ii) On estimation of amine at the close of expt. (in a separate expt.) all the amine was found unreacted.
10	"	2N-H <sub>2</sub> SO <sub>4</sub>	"	11.0	10.56	3.0 (0.35)	7.09 (10.55)	
11	"	"	"	7.9	—	10.1 (0.8)	89.9 (7.1)	The mercury was covered by a column of CCl <sub>4</sub> .

*Interaction of Nitrous Acid and Methylamine : Influence of Acid Concentration\*.*—

The experiments were carried out with mg. molar quantities of the reactants. These were left mixed up in test tubes for a period of 24 hours at the end of which the residual methylamine in these was estimated (Table IV)\*\*.

TABLE IV

Expt. No.	Reactants.	Medium.	Dilution.	Methylamine decomposed (%)	
				5	
1	Me. NH <sub>2</sub> , HCl and HNO <sub>2</sub> in 1:1 ratio.	Acetic acid	5 c.c.	(i)	44.0
		6%		(ii)	42.0
2	"	10 "	"	(i)	40.0
				(ii)	38.0
3	"	20 "	"	(i)	36.0
				(ii)	35.0
4	"	40 "	"	(i)	26.0
				(ii)	26.0
5	"	66 "	"	(i)	20.0
				(ii)	21.0
6	"	2N-H <sub>2</sub> SO <sub>4</sub>	"	(i)	2.0
				(ii)	4.0

\* Vide Fig. 3.

\*\* In a couple of experiments, separately carried out using larger quantities of the reactants (10 mg. moles each), the contents were tested for the presence of formaldehyde, formic acid and sym-dimethylhydrazine as possible oxidation products of methyl alcohol or methylamine, but none was detected.

*Interaction of Nitrous Acid with Methylamine, Ammonium Chloride and Thiocarbamide.\**—Influence of the acid concentration of the medium on the progress of the reaction as indicated by the proportion of nitrogen in the evolved gases is shown below.

TABLE V

Medium.	% N <sub>2</sub> **from NH <sub>4</sub> Cl.	% N <sub>2</sub> from MeNH <sub>2</sub> ,HCl	% N <sub>2</sub> from thio-carbamide.	% Methylamine decomposed. (in test tubes)
I	2	3	4	5
6% Acetic acid.	77.7	75.5	82.4	83.0
10 „ „		74.7	84.7	39.0
20 „ „	60.8	65.3	79.6	35.5
40 „ „	50.7	61.1	77.3	26.0
66 „ „	46.4	50.0	68.1†	20.5
2N-H <sub>2</sub> SO <sub>4</sub>	15.8	3.0	3.5	3.0

(Vide Fig. 3, curves 1, 2 and 3).

\* Experiments with methylamine hydrochloride, and ammonium chloride were allowed to proceed for 24 hours (and were yet incomplete), but those with thiocarbamide were complete within a few minutes.

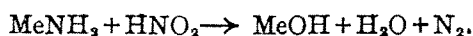
\*\* Only percentages of N<sub>2</sub> are shown, the rest of the gas was nitric oxide.

† In the case of thiocarbamide the medium contained 80% acetic acid.

## DISCUSSION

Mainly two reactions appear to be taking place in the nitrometer :

(i) The amine-nitrous acid interaction according to the equation



(ii) The spontaneous or self decomposition of nitrous acid, presumably, according to some such process as  $3\text{HNO}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$ .

The progress of (i) is indicated by the amount of nitrogen formed, and of (ii) by that of nitric oxide. That the nitrogen is exclusively a product of (i) is well indicated by the results of Expts. 1 and 10 (Table III, column 9).

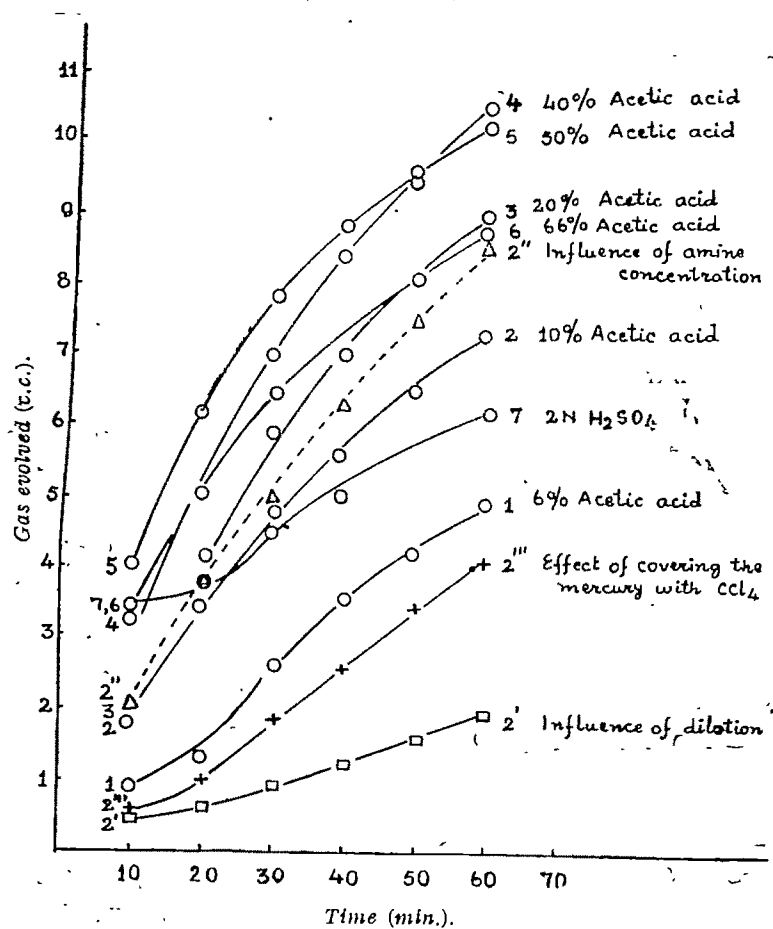
As judged by the composition and quantities of gas evolved (vide Tables I-III), interaction of methylamine and nitrous acid is incomplete even after 24 hours. The reaction is very much faster in the initial stages as indeed is to be anticipated owing to the larger concentration of the reactants then available. A comparison of the results in Tables II and III (column 6) indicates that almost 50% of the total reaction undergone in 24 hours, is complete within first 60 minutes of starting the reaction. It is clear therefore that any conclusions with respect to the influence of the factor under consideration would be nearer the truth, if they are drawn from the progress of the reaction in the first hour of the change (vide Table II).

The influence of acid concentration on (i) the amine-HNO<sub>2</sub> interaction, (ii) the self

decomposition of nitrous acid, and (iii) the overall change comprising (i) and (ii), is illustrated by the volumes of nitrogen, nitric oxide, and the total gas evolved, shown in columns 7, 8 and 5-6 respectively of Table II (also vide Table III). It will be seen that the (i) is favoured by the increasing acid concentration up to a critical value, any increase beyond which affects the reaction velocity adversely and may even completely suppress the reaction. The change (ii) also shows at first a rapid and then a more gradual increase in the reaction rate; beyond a certain critical concentration of the acid, this change appears to indicate a sort of saturation effect in its velocity. The overall reaction velocity, as is to be expected on the basis of the individual trends of (i) and (ii), shows an increase at first and then a continuous and gradual decline. These results are graphically represented in Figs. 1 and 2.

FIG. 1

*Interaction of  $\text{HNO}_2$  with methylamine*  
(Vide Table II)

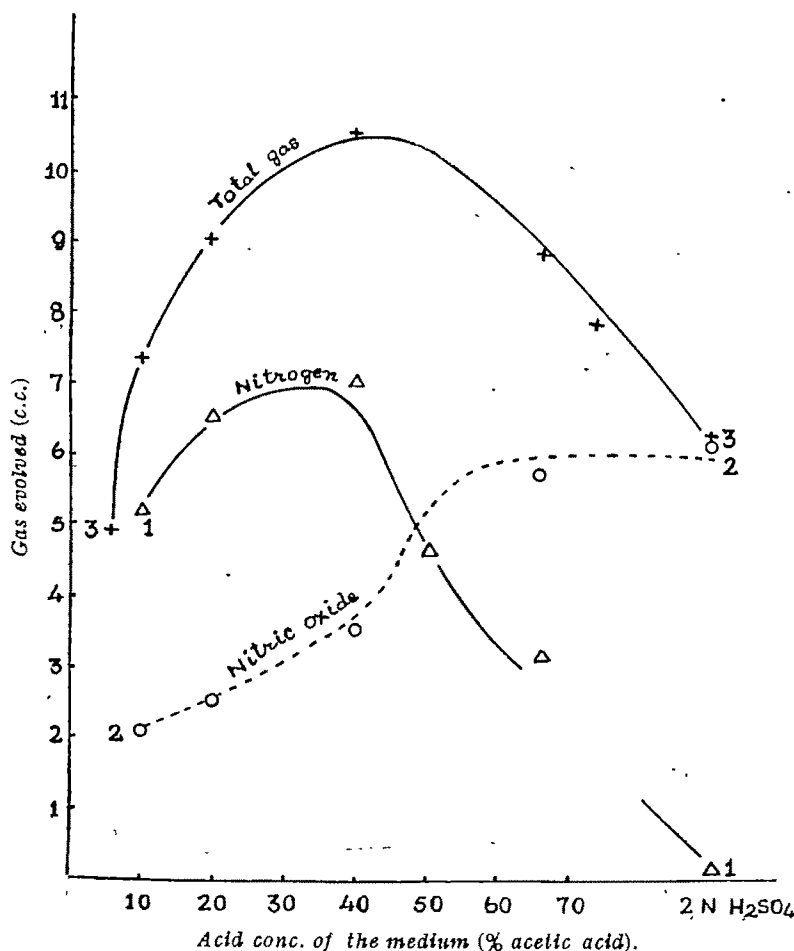


Curve 1-7—influence of acid conc.

Curves 2' 2'', 2'''—influence of other factors on the velocity of the changes



FIG. 2  
Interaction of nitrous acid & methyl amine.  
(Vide Table II)



The above observations are in agreement with the earlier findings (Adamson and Kenner, *J. Chem. Soc.*, 1934, 838 ; Taylor, *ibid.*, 1928, 1099 ; Krall, this *Journal*, 1939, 16, 9) : (a) That a certain amount of free acid is essential for the occurrence of amine-nitrous acid interaction which is suppressed by the presence of excessive mineral acid and (b) that the self decomposition of nitrous acid is favoured in a strongly acidic medium. With respect to the latter change, the tendency at high acid concentrations towards a saturation effect in its velocity, as evinced by curve 2 of Fig. 2, is, indeed, remarkable and does not appear to have been noted earlier.

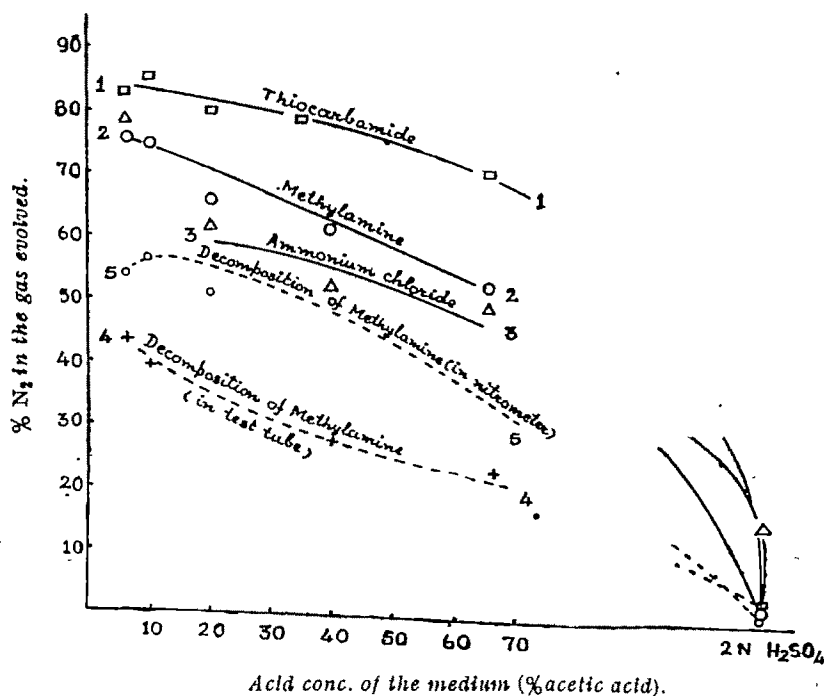
The occurrence of a critical acid concentration ( $p_n$ ) for the optimum amine-nitrous acid interaction (for a given set of conditions) recalls of a similar phenomenon in the hydrolysis of amides which has been attributed to the formation of the salt of the amide in presence of a large excess of acid, the salt being incapable of hydrolysis (Sidgwick, Taylor and Baker, "The Organic Chemistry of Nitrogen" Oxford, 1942, p. 145). Further, it has been clear from the chemistry of

numerous amino compounds that a positively charged amino group behaves differently from an uncharged or weakly charged amino group (Sidgwick, Taylor and Baker, *loc. cit.*, pp. 62, 69, 135, 256, 391). The markedly differential behaviour of nitrous acid towards the amine in weak and strong acid media, observed in the present experiments, no doubt, arises due to the strong or weak polarity developed by the amino group under the respective conditions. It is not unlikely that much of the apparent complexity of the interaction of amino compounds with nitrous acid, in general, might be due to an inadequate recognition of this influence of hydrogen-ion concentration of the medium.

The mercury of the nitrometer has a catalysing influence on both the changes (vide Fig. 3, curves 4 and 5, and Expt. Nos. 2 and 5 of Table II, and Expt. Nos. 3 and 4, and 10 and 11 of Table III). The influence of dilution and of amine concentration is as expected; the former slows down the reaction while the latter speeds it up (vide Expt. Nos. 2-3, and 2-4 of Table II).

FIG. 3

Interaction of  $\text{HNO}_2$  with thiocarbamide, methylamine and  $\text{NH}_4\text{Cl}$



For curves 1-3, vide Table V.

" 4 " " " IV

5—figures calc. from Table III.

The results with ammonium chloride and thiocarbamide show a general similarity with those with amine (vide Table V; Fig. 3, curves 1, 2 and 3). But in the case of thiocarbamide the reaction is characterised by the fact that it is very rapid as compared to that with  $\text{NH}_4\text{Cl}$  and  $\text{CH}_3\text{NH}_2$ .  $\text{HCl}$  and is completed within half

an hour. Secondly, the nitric oxide evolved in this case is not due to the self decomposition of  $\text{HNO}_2$ , but is formed by a specific oxidation reaction of the thiocarbamide (Werner, *loc. cit.*, 1912). The reaction velocities of these three compounds with nitrous acid can be roughly represented in the order :

Thiocarbamide > methylamine > ammonium chloride (vide Fig. 3, curves 1, 2 and 3 ; cf. Taylor).

On the above results therefore it is suggested that the suppression of the  $\text{NH}_2\text{—HNO}_2$  reaction at high acid concentrations (low  $p_H$  of the media) in the case of the amines, and its diversion through other channels in the case of thiocarbamide arises from the same cause viz., locking up of the amino group by salt formation.

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DEPARTMENT OF CHEMISTRY,  
COLLEGE OF SCIENCE,  
BANARAS HINDU UNIVERSITY.

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## THIOCYANAMIDES AND SULPHONITRILES : THEIR CONSTITUTION AND IDENTITY

BY R. H. SAHASRABUDHEY

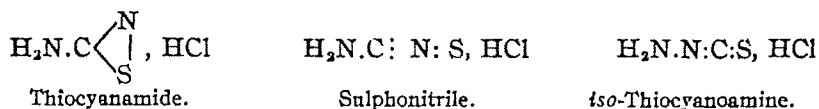
It has been shown that the thiocyanamide of Freund and Schander and aromatic sulphonitriles of Oliveri-Mandala are identical with formamidine disulphide and the corresponding aminoarylthiazoles respectively.

Freund and Schander (*Ber.*, 1896, 29, 2500) by the action of concentrated hydrochloric acid on 'amidothiotriazole' obtained the hydrochloride,  $\text{CSN}_2\text{H}_2\text{Cl}$  of a base which they called thiocyanamide. Later, Oliveri-Mandala (*Gazzetta*, 1914, 44, 670) showed that the 'amidothiotriazoles' were really thiocarbamic acid azides, and by the action of hydrochloric acid on phenyl-, tolyl- and ethyl-thiocarbamic acid azides prepared the salts of the corresponding thiocyanamides which he called sulphonitriles :



No attempt seems to have been made by him or by any other worker to prepare the parent thiocyanamide, viz.  $\text{CSN}_2\text{H}_2\text{Cl}$  of Freund and Schander, or to examine its constitution. The generic relationship obtaining between the thiocyanamides and the sulphonitriles i.e., the proved identity (i) of Freund's triazoles and tetrazoles (*Ber.*, 1895, 28, 74 ; 1896, 29, 2491) with the azides obtained by Oliveri-Mandala (*loc. cit.*) and (ii) of ethylthiocyanamide (*Gazzetta*, 1922, 52, 98) obtained by both the workers, rendered such an enquiry apparently unnecessary.

Freund and Schander have discussed the constitution of thiocyanamide for which they favoured a three membered ring structure (*loc. cit.*). Oliveri-Mandala represented it as a sulphonitrile, while more recently (Adams, "Organic Reactions," Vol. III, 1946, p. 362) it has been given the constitution of an isothiocyanoamine : Thus

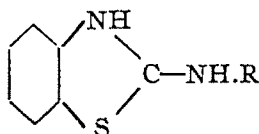


These constitutions have been built up from an erroneous composition assumed for the compound to suit the mechanism of its formation as laid down by Freund and Schander, and by Oliveri-Mandala. Analytically determined, the hydrochlorides of thiocyanamide and its methyl homologue have the composition  $\text{CSN}_2\text{H}_4\text{Cl}$  and  $\text{C}_2\text{SN}_2\text{H}_6\text{Cl}$  respectively and not  $\text{CSN}_2\text{H}_3\text{Cl}$  or  $\text{C}_2\text{SN}_2\text{H}_5\text{Cl}$  as hitherto assumed (Freund and Schander, *Ber.*, 1896, 29, 2504, 2499). Further, these formulations do not take into account the fact that free bases of these salts, excepting those from aromatic thiocyanamides, have been shown incapable of free existence.

Formation of thiocyanamide from thiocarbamic acid azide and the identity of its composition with the empirical composition of formamidine disulphide (hydrochloride,  $\text{CSN}_2\text{H}_4\text{Cl}$ ), the oxidation product of thiocarbamide, suggested to the author that they might be identical.

The expectation has been fully realised. This, however, in the opinion of the author, does not settle the question of its constitution which is being examined separately.

The constitution of the aromatic thiocyanamides or sulphonitriles cannot be identical with the corresponding formamidine disulphides, because aryl derivatives of the latter are known not to exist, whilst free bases from the salts of the former have been prepared and even their molecular weights determined. The structure assigned to them by Oliveri-Mandala (*loc. cit.*, 1922), since it assumes a penta-covalent nitrogen, is clearly untenable. In the light of the work of Fischer and Besthorn (*Annalen*, 1882, **212**, 316) and Hegershoff (*Ber.*, 1903, **36**, 3134), it appears more than probable that they are identical with the corresponding aminoarylthiazoles :



where R is a hydrogen atom or an alkyl residue. A comparison of the melting points given by Oliveri-Mandala (*loc. cit.*) with those of the corresponding arylaminothiazoles almost proves their identity :

Aniline sulphonitrile ( $\text{C}_7\text{H}_6\text{N}_2\text{S}$ ), m.p.  $122-123^\circ$  ; aminobenzthiazole ( $\text{C}_7\text{H}_6\text{N}_2\text{S}$ ), m.p.  $123^\circ$  ; *o*-toluidine sulphonitrile ( $\text{C}_8\text{H}_8\text{N}_2\text{S}$ ), m.p.  $138-40^\circ$  ; amino-*o*-toluthiazole ( $\text{C}_8\text{H}_8\text{N}_2\text{S}$ ), m.p.  $140^\circ$ .

#### EXPERIMENTAL

*Preparation and Properties of Thiocyanamide.*—Thiocyanamide hydrochloride was prepared from 'amidothiotriazole' by Freund and Schander's procedure (*loc. cit.*).

Its saline character is evident from its easy solubility in water and alcohol and insolubility in ether, chloroform, carbon tetrachloride and benzene. Its aqueous solutions are highly acid due to hydrolysis. Free base cannot be isolated from it, but on addition of alkali to its solutions sulphur is precipitated and thiocarbamide and cyanamide are formed in solution. The thiocyanamide salts liberate iodine from aqueous potassium iodide solutions.

*Reduction of Thiocyanamide Hydrochloride.*—On reduction of an aqueous solution of thiocyanamide hydrochloride with zinc and hydrochloric acid, large quantities of hydrogen sulphide were evolved and some free sulphur deposited. The solution was filtered free from sulphur and a part of it treated with excess of NaOH solution when no precipitation of sulphur was observed, indicating the absence of unreduced thiocyanamide. The rest of the solution was then made ammoniacal and zinc precipitated as  $\text{ZnS}$  with hydrogen sulphide and filtered out. The filtrate thus freed from sulphur, zinc salts

and thiocyanamide on concentration deposited crystals of thiocarbamide in a syrupy residue which proved to be cyanamide.

*Identity of Thiocyanamide Salts with Formamidine Disulphide Salts.*—The nitrate, picrate, and the hydrobromide of thiocyanamide were prepared by treating the aqueous solutions of its hydrochloride with the appropriate acids: Hydrochloride, m.p.  $186^{\circ}$  (d); hydrobromide, m.p.  $185-190^{\circ}$  (d); nitrate, m.p.  $82^{\circ}$  or  $140^{\circ}$  (d); picrate, m.p.  $154^{\circ}$  or  $164^{\circ}$  (d).

The melting points of the various salts, as will be evident, are identical with those of the corresponding salts of formamidine disulphide (*Proc. Indian Sci. Cong.*, 1948, Part III, p. 25). On determining the melting points of the mixtures of the respective salts from both the sources no depression was recorded, confirming their identity.

The author wishes to express his sincere thanks to Prof. H. Krall for his interest and to Principal S. S. Joshi and Prof. P. S. Varma for the facilities.

DEPARTMENT OF CHEMISTRY,  
COLLEGE OF SCIENCE,  
BANARAS HINDU UNIVERSITY.

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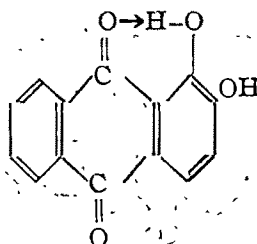
## THE PREFERENTIAL ACYLATION OF $\beta$ -HYDROXYL GROUP IN 3-NITROALIZARIN

BY R. GONSALVES, A. N. KOTHARE AND V. V. NADKARNY

An additional experimental evidence has been put forth in support of the preferential acylation of  $\beta$ -hydroxy group in the alizarin molecule.

It has been reported by Dimroth, Friedman and Kammerer (*Ber.*, 1920, 53, 481) that it is possible to acylate the  $\beta$ -hydroxyl group without affecting the  $\alpha$  one, by using moderate conditions of experiment. It is a question of relative rates; the acetylation of the  $\alpha$ -hydroxyl group is more sluggish than that in  $\beta$  position. It is also known that the OH group in  $\alpha$ -position cannot be readily alkylated by the usual alkylating procedures. The methylation of the  $\alpha$ -OH group can be effected only by heating the dry K-salt with dimethyl sulphate. Methylation of the  $\alpha$ -OH group is known to be greatly facilitated by first reducing the anthraquinone system and then methylating the "leuco" compound by the normal methods.

The observed inactivity of the  $\alpha$ -OH group may be due to chelation, H of OH sharing the electron pair of the O of CO group:

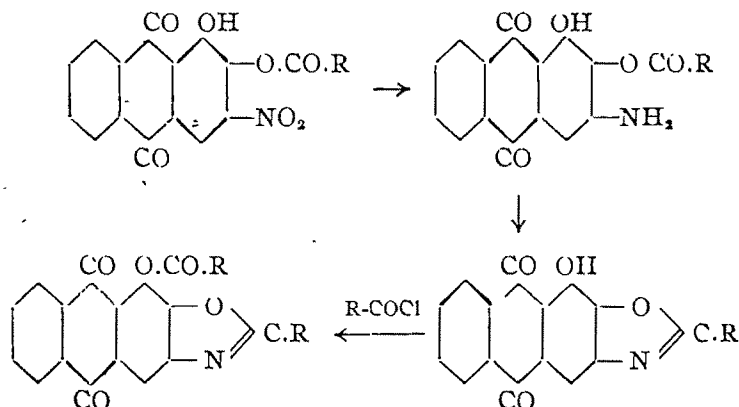


The observed increased activity of the leuco derivative (in the leuco, CO is changed to -C-OH and no chelation is possible) greatly supports such an assumption.

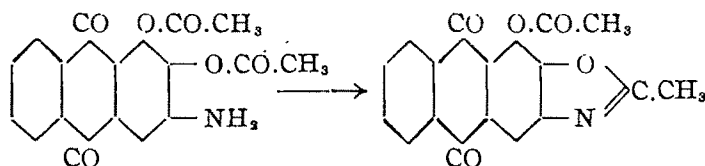
We have been able to put forward additional evidence that a  $\beta$ -hydroxy group is preferentially acylated under moderate conditions of working. Thus, we have acylated (acetylated and benzoylated) 3-nitroalizarin in pyridine at 100°, using equimolar quantities of the acyl chloride and the nitroalizarin. The acyl derivative formed in either case was found to be the 2-acyl-3-nitroalizarin. This has been established in the following way:—

1. The analytical results show that the compounds obtained on acylation are mono-acyl derivatives.

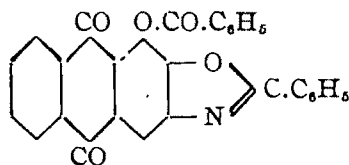
2. The mono-acyl derivative is reduced with zinc dust and 50% acetic acid to the corresponding amine; the latter is then refluxed with  $P_2O_5$  in toluene when an oxazole derivative is formed which is further acylated (acetylated, and benzoylated) to give a known oxazole derivative.



The acetyl compound shows no depression of m.p. when mixed with a small quantity of the compound obtained from 1:2-diacetyl-3-aminoalizarin by refluxing with  $P_2O_5$  in toluene.



Similarly, the final product with monobenzoyl-3-nitroalizarin would be



which has been found to be the actual case. It is identical with the compound obtained by refluxing of the 1:2-dibenzoyl-3-aminoalizarin with  $P_2O_5$  in toluene.

#### EXPERIMENTAL

*Preparation of 2-Acetyl-3-nitroalizarin (I).*—3-Nitroalizarin (5 g.) was dissolved in warm pyridine (50 ml.) kept in a round-bottomed flask (250 ml. capacity) and fitted with a condenser. To this solution acetyl chloride (1.5 ml., slightly more than equimolar quantity) was added. The reaction was allowed to proceed on a water-bath at  $100^\circ$  for 8 hours, and then allowed to stand for 24 hours. No derivative crystallised out. However, on pouring the reaction mixture into 200 ml. of water, the acetyl derivative separated out. It was collected at the pump, washed with water several times and dried. It was finally crystallised from benzene in orange needles, m.p.  $231^\circ$ , yield 83%. (Found: C, 59.11; H, 3.03; N, 4.12.  $C_{16}H_9O_7N$  requires C, 58.71 H, 2.76; N, 4.28 per cent).



*Reduction of (I) to 2-Acetyl-3-aminoalizarin.*—The compound (I, 5 g.) was dissolved in 50% acetic acid (60 ml.) kept in a conical flask. To the warm solution zinc dust (3 g.) was added (a little quantity at a time) with vigorous shaking of the mixture. The contents of the flask became gradually deep red. The reaction flask was then placed in a water-bath at 50° for one hour, and the warm solution quickly filtered. The filtrate was diluted with water when the amino compound separated out. It was collected, washed free from acid with water, dried and finally crystallised from alcohol in red needles, m.p. 217°.

*Oxazole Ring Formation.*—2-Acetyl-3-aminoalizarin (3 g.) and  $P_2O_5$  (1 g.) were added to dry toluene (40 ml.) and the reaction mixture boiled under reflux for 3 hours. It was then allowed to cool when the oxazole derivative separated out. It was collected at the pump, washed free from toluene with ether and then with water from the phosphorus compounds and finally dried, when yellowish brown needles melting at 236° were obtained in 65% yield (Found C, 68.30; H, 3.52; N, 4.88.  $C_{16}H_9O_4N$  requires C, 68.81; H, 3.22; N, 5.01 per cent). The compound is soluble in  $Na_2CO_3$  and NaOH solutions in the cold giving violet solutions. It dissolves in concentrated  $H_2SO_4$  with orange colour.

On acetylation by the usual procedure, a product was formed which on crystallisation from benzene was identical with the oxazole obtained from 1:2-diacetyl-3-aminoalizarin, by refluxing with  $P_2O_5$  in toluene.

*Preparation of Oxazole from 1:2-Diacetyl-3-nitroalizarin: (a). Preparation of 1:2-Diacetyl-3-nitroalizarin.*—To 3-nitroalizarin (10 g.), dissolved in hot nitrobenzene (50 ml.), a large excess of acetyl chloride (12 ml.) was added and the reaction mixture refluxed on a sand-bath for 6 hours. On cooling, the diacetyl derivative crystallised out. It was collected at the pump and washed free from nitrobenzene with petrol as yellow needles, m.p. 218°, yield 80%.

(b). *Reduction of 1:2-Diacetyl-3-nitroalizarin* was carried out by using the same procedure as in the case of 2-acetyl-3-nitroalizarin, described above. The product was crystallised from glacial acetic acid, m.p. at 240°.

(c). *Oxazole formation* was carried out in the same way as described above in the case of 2-acetyl-3-aminoalizarin. The product formed light brown needles, m.p. 268°, yield 68%. (Found: C, 67.80; H, 3.60; N, 4.42.  $C_{16}H_{11}O_5N$  requires C, 67.29; H, 3.42; N, 4.36 per cent).

*Preparation of 2-Benzoyl-3-nitroalizarin.*—The method employed is essentially the same as in the acetylation; benzoyl chloride (28 ml.) was used in place of 1.5 ml. of acetyl chloride. The product on crystallisation from nitrobenzene formed orange coloured needles, m.p. 302°, yield 79%.

*Reduction of 2-Benzoyl-3-nitroalizarin.*—The nitro compound was reduced with zinc dust and acetic acid as in the case of the corresponding acetyl derivative. On crystallisation from alcohol it formed deep orange needles, m.p. 254°.

*Oxazole formation* was effected in the same way as that used in the case of the corresponding 2-acetyl-3-aminoalizarin. The compound was crystallised from alcohol, m.p. 278°, yield 70%.

It dissolves in sodium carbonate and caustic alkali and gives a violet solution. With concentrated  $H_2SO_4$ , it gives an orange coloured solution. (Found: C, 74.31; H, 3.36; N, 4.29.  $C_{21}H_{11}O_4N$  requires C, 73.90; H, 3.32; N, 4.10 per cent). On benzoylation by the usual procedure, a product was formed which on crystallisation from benzene was found to be identical with the oxazole obtained from 1:2-dibenzoyl-3-aminoalizarin by refluxing with  $P_2O_5$  in toluene.

*Preparation of Oxazole from 1:2-Dibenzoyl-3-nitroalizarin:* (a). *Preparation of 1:2-Benzoyl-3-nitroalizarin.*—This was obtained by the same procedure as in the preparation of the diacetyl derivative using 20 ml. (excess) of benzoyl chloride in place of acetyl chloride. The product was freed from traces of benzoic acid by repeated washing with water, m.p.  $276-78^\circ$ , yield 85%.

(b). *Reduction of 1:2-Benzoyl-3-nitroalizarin.*—Procedure was the same as under the corresponding 1:2-diacetyl derivative. The product on crystallisation from glacial acetic acid gave yellow leaflets, m.p.  $247^\circ$ .

(c) *Oxazole formation.*—Same procedure as in the case of the 1:2-diacetyl-3-aminoalizarin was adopted. The product formed light grey shining needles, not melting below  $310^\circ$ , yield 71%. (Found: C, 75.19; H, 3.78; N, 3.30.  $C_{28}H_{18}O_5N$  requires C, 75.51; H, 3.37; N, 3.14 per cent).

DEPARTMENT OF CHEMISTRY,

ST. XAVIER'S COLLEGE, BOMBAY I.

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STUDIES IN FRIES MIGRATION. PART V. THE FRIES MIGRATION  
OF MONOMETHOXYQUINOL ESTERS AND 4-BENZOYLOXY-  
QUINOL ACETATE

BY GUNVANTIAL CHANDULAL AMIN AND NARSINH MULJIBHAI SHAH

The Fries migration of monomethoxyquinol acetate and benzoate has been systematically investigated for the first time. The acetate gives 5-methoxyquinacetophenone in small quantity accompanied with a large amount of quinacetophenone, the demethylation taking place during the migration. In case of the benzoate, the migration is complicated; several products—quinol mono- and dibenzoates, monobenzoylquinbenzophenone and benzoic acid, are obtained. It appears that the demethylation first takes place, the course of the migration then being nearly analogous to that of quinol monobenzoate as already described in Part III of this series. 4-Benzoyloxyquinol acetate forms monobenzoylquinacetophenone and quinacetophenone along with quinol dibenzoate and benzoic acid. No diketone could be isolated.

In extension of our work on the Fries migration of quinol esters, described in an earlier part of this series (Part III, this *Journal*, 1948, 25, 377), we have now investigated the Fries migration of monomethoxyquinol acetate as well as benzoate.

The perusal of literature shows that the Fries migration of monomethoxyquinol esters has been hardly attempted. Recently, however, Cook, Heilbron and Lewis (*J. Chem. Soc.*, 1942, 659) found that monomethoxyquinol palmitate and stearate did not migrate under the conditions of the Fries reaction.

The present work on the migration of the acetate (I,  $R = \text{COMe}$ ) was undertaken (i) as a part of the comprehensive study of the migration of quinol esters and (ii) to find whether it can be used as a direct method of preparing difficultly accessible monomethoxyquinacetophenone (II,  $R = \text{H}$ ). It has been found that the migration takes a normal course but the formation of the expected monomethoxyquinacetophenone is not satisfactory, as a good quantity of the product is demethylated to quinacetophenone, the separation being effected by steam-distillation when the monomethoxy derivative is carried over by steam.

The above migration was investigated at different temperatures. To avoid repetitions, the results are summarised in Table I. It is clear from the results that the yield of the monomethoxyquinacetophenone decreases as the temperature at which the migration is carried out is raised.

The isomerisation of the benzoyl ester (I,  $R = \text{COPh}$ ) was found to be interesting. Instead of the expected monomethoxyquinbenzophenone and/or quinbenzophenone by analogy with the acetate, described above, quinol dibenzoate was found to be the main product accompanied with its monobenzoate. It appears that the methoxy group is first eliminated; subsequently the compound behaves as quinol monobenzoate, whose migration has been already described (Part III, *loc. cit.*). The migration was investigated under various conditions, the results being summarised in Table II.

The Fries migration of 4-benzoyloxyquinol acetate (III) was undertaken as it contains two different acid residues viz., acetyl and benzoyl, both being capable of undergoing the migration, and hence interesting products could be expected.

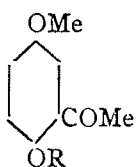
The migration at 98° gave only the traces of quinol mono- and dibenzoates along with the unchanged ester. It appears that the acetyl group is less firmly held than the benzoyl one (cf. Rosenmund and Schnuur, *Annalen* 1928,, 461, 56).

At 125°-130° quinacetophenone, traces of quinol dibenzoate, benzoic acid and a colorless product (m.p. 77-78°) were isolated from the reaction mixture. It has been assigned the constitution of monobenzoylquinacetophenone (IV, R = H) as (i) it is soluble in alkali and further, it gives ferric chloride colour test indicating -OH and -COMe groups in *ortho* positions, (ii) on hydrolysis by (conc.) sulphuric acid, it gives quinacetophenone, identified by mixed melting point, and (iii) it gives a benzoyl derivative, identical with quinacetophenone dibenzoate on direct comparison. The migration at 150°-155° gave also the similar results with variation in yields. Thus, at higher temperatures both the groups are affected, since products involving the migration of both the acid residues are obtained.

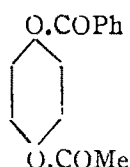
The above results point out that the acetyl group migrates more easily than the benzoyl one, which is more firmly held to the oxygen atom. It is interesting to note that quinol dibenzoate is also formed as one of the products (cf. Part III).



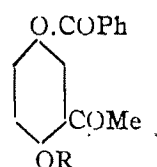
(I)



(II)



(III)



(IV)

#### EXPERIMENTAL

*Monomethoxyquinol* (I, R=H) was prepared according to Robinson and Smith (*J. Chem. Soc.*, 1926, 393). The product distilled at 243°-246° solidifying to fibrous needles, m.p. 53-54° (50 g. from 110 g. of quinol).

*Monomethoxyquinol acetate* (I, R=COMe) was prepared by sodium acetate-acetic anhydride method by heating for 3 hours on a water-bath. On usual treatment with water an oil separated. It was dried and distilled at 235°-236°; the distillate did not solidify even on cooling. It does not give any colour with alcoholic ferric chloride. (Found: C, 64.9; H, 6.1.  $C_9H_{10}O_3$  requires C, 65.0; H, 6.0 per cent).

*Fries Migration of (I).*—The acetate (3.3 g., 1 mol.) and anhydrous aluminium chloride (8.8 g., 3.3 mols.) were carefully mixed and heated at 60-65° on a water-bath for 1 hour. As the green pasty product obtained by decomposing the reaction mixture by ice and hydrochloric acid (conc., 5 c.c.) could not be satisfactorily crystallised, it was steam-distilled till no oily drops came over. The ether extraction of the distillate gave a green product, which was crystallised from dilute methyl alcohol as small needles, m.p. 50-51° (0.8 g.). It was identified as quinacetophenone monomethyl ether

(II, R=H) by the mixed melting point with an authentic sample prepared according to Kostanecki and Lampe's method (*Ber.*, 1904, **37**, 774).

The residual liquid in the distilling flask on cooling gave a brown product which crystallised from water as greenish needles, m.p. and mixed m.p. with quinacetophenone, 201-202° (0.8 g.). A small quantity of a tarry residue was obtained after separation of quinacetophenone.

The *benzoyl derivative* (II, R=COPh) of monomethoxyquinacetophenone was prepared by benzoyl chloride-pyridine method, as colorless silky needles from alcohol, m.p. 61-62°. It is insoluble in sodium hydroxide. (Found: C, 71.1; H, 4.9.  $C_{16}H_{10}O_4$  requires C, 71.1; H, 5.2 per cent).

Other typical experiments carried out with the same amount of reactants, and the period of heating (one hour) are tabulated below.

TABLE I

Expt. No.	Temp.	Solvent.	Quinacetophenone.	5-Methyl ether
1	95-98°	—	0.8 g.	0.6 g.
2	130°	—	1.2	—
3	60-70°	Nitrobenzene (50 c.c.)	—	—
4	25-30°	(24 hrs.)	—	—

*Monomethoxyquinol benzoate* (I, R=COPh) was prepared by Schotten-Baumann method as lustrous needles, m.p. 85-86°. It melts to a cloudy liquid which becomes clear at 109°-110°. It appears that it exists in the 'mesomorphic' state between the range 85° and 110° (vide Glasstone, "Physical Chemistry", p. 514).

The Fries migration of this ester was carried out similarly as that of quinol mono- or dibenzoate, already described in Part III. The separation of the different products obtained was also done similarly as before. The results are summarised in the following table.

TABLE II

Monomethoxyquinol benzoate = 3.4 g. (1 mol.).  $AlCl_3$  = 6.6 g. (3.3 mols.).  
Reaction period = 1 hour.

Expt. No.	Temp.	Quinol monobenzoate.	Quinol dibenzoate.	Monobenzoyl-quinbenzophenone.
1	95-98°	0.1 g.	0.7 g.	—
2	130-132°	0.5	0.5	0.3 g.
3	150-155°	Traces	0.4	0.3
4	30-35°	—	—	—

Notes: (1) In expt. 1, a trace of benzoic acid and the unchanged ester (0.8 g.) were obtained.

(2) In expt. 4, nitrobenzene (40 c.c.) was used and the reaction mixture left overnight; no crystalline product could be obtained on working up the reaction mixture

(3) In all experiments, a variable amount of pasty mass was obtained.

*4-Benzoyloxyquinol acetate* (III) was prepared by sodium acetate-acetic anhydride method from quinol monobenzoate (three hour's heating on a water-bath) as lustrous

leaflets from dilute alcohol (50%), m.p. 124-25°. It gives no colour with alcoholic ferric chloride. (Found: C, 70.4; H, 4.8.  $C_{15}H_{12}O_4$  requires C, 70.3; H, 4.7 per cent). The same compound could be obtained by using a few drops of pyridine instead of sodium acetate.

*Fries Migration of (III).*—(a). The mixture of the ester (III, 3.8 g., 1 mol.) and aluminium chloride (6.7 g., 3.3 mols.) was heated at 95°-98° on a water bath for 1 hour. On decomposing the reaction mixture as usual, a brown solid was obtained which was dissolved in alcohol for crystallisation; a small insoluble residue remaining over was identified as quinol dibenzoate by mixed melting point. The alcoholic filtrate gave mostly the unchanged ester (3 g.). After its separation, the residual mother-liquor was extracted with dilute sodium hydroxide (2%); on acidification it gave traces of quinol monobenzoate, m.p. and mixed m.p., 162-63°.

(b). The above migration was carried out at 125°-130° for 1 hour, and worked up as before. A trace of quinol dibenzoate was obtained as an alcohol-insoluble residue.

The alcoholic solution gave a product of indefinite melting point (68°-110°), which on extraction with dilute sodium bicarbonate (5%) gave traces of benzoic acid. The residual brown product on extraction with dilute alkali gave a solid which after two crystallisations from alcohol gave colorless needles, m.p. 77-78° (0.5 g.). (Found: C, 70.2; H, 4.8.  $C_{16}H_{12}O_4$  requires C, 70.3; H, 4.7 per cent). It gives deep yellow colour with alkalis or conc. sulphuric acid and intense red colour with alcoholic ferric chloride. It has been identified as monobenzoylquinacetophenone (IV, R=H).

The remaining alcoholic mother-liquor after separation of the above compound was diluted and extracted with hot water repeatedly. The aqueous extract on cooling gave greenish needles of quinacetophenone, m.p. and mixed m.p., 201-202° (0.5 g.).

(c). The reaction was carried out at 150°-155° and the products were separated as in (b). They were benzoic acid (0.3 g.), quinol dibenzoate (0.2 g.), monobenzoylquinacetophenone (0.5 g.) and quinacetophenone (0.3 g.).

In all the above experiments a small amount of uncrystallisable brown residue was always left over after the isolation of the crystalline products.

The *hydrolysis of monobenzoylquinacetophenone* (0.5 g.) (IV, R=H) by sulphuric acid (conc., 5-7 c.c.) at room temperature for 20-24 hours gave quinacetophenone, identified by the mixed melting point.

The *benzoyl derivative* (IV, R=—COPh) was prepared by benzoyl chloride-pyridine method as needles from alcohol, m.p. 113-14°. The mixed melting point with an authentic sample, prepared by the benzoylation of quinacetophenone, was undepressed.

The *acetyl derivative* (IV, R=COMe) was prepared by sodium acetate-acetic anhydride method and crystallised from alcohol as colorless needles, m.p. 76-77°. The mixed melting point with the original ketone was depressed to 58-60°. (Found: C, 68.4; H, 4.9.  $C_{17}H_{14}O_4$  requires C, 68.4; H, 4.8 per cent).

The *semicarbazone* was obtained as colorless needles from alcohol, m.p. 245-47° (decomp.).

## PREPARATION OF ANTIBACTERIALS FROM ORGANO-MERCURIALS. PART II

By S. S. GUHA SIRCAR AND KHIROD KUMAR PATNAIK

Fourteen substituted phenylurea and 12 substituted phenylthiourea derivatives have been prepared. All members of the former and 4 members of the latter group were mercurated. The bactericidal action of the two original groups of compounds and that of the mercurated ureas were studied against *B. Coli*. They have fairly high activities, especially acetoxymercuri-*p*-chlorophenylurea and diacetoxymercuri- $\alpha$ -naphthylurea, which are active in dilutions of 1:140,000 and 1:160,000 respectively. The mercurated phenylthioureas being unstable to heat and light are not useful.

In Part I of this series (this *Journal*, 1950, 27, 357) the preparation and properties of a series of organo-mercurials derived from some substituted phenoxyacetic acids and from some phenylglycine derivatives were described. Some of these had quite high bactericidal activities *in vitro*. In the present paper the preparation and bactericidal investigation of a number of substituted phenylureas, phenylthioureas and also of a series of mercurated phenylureas have been examined. The introduction of mercury in the molecule in the form of one or two acetoxy-mercuri groups, has been found to increase many times the bactericidal action in all cases. The mercurated thioureas, however, have been proved to be unstable to moderate heat and to light, and are, besides, sparingly soluble in water. These facts prevented a biological study being made with them.

Most of the phenylureas (except the carboxyphenyl derivatives) are already known and are prepared by the action of either urea or KCNO solution on the hydrochlorides of the aromatic primary amines. The thioureas could be prepared by two available methods: using KCNS on the hydrochlorides of the bases, or by the addition of ammonia to the phenyl mustard oils, which were themselves prepared from the ammonium dithiocarbamates of the bases.

The only reference available in the literature of the mercuration of compounds similar to the phenylureas seems to be the work of Shah (this *Journal*, 1938, 18, 149).

The mercuration of the ureas was carried out in the cold or at the ordinary temperature in dilute alcohol or acetic acid solution by mercuric acetate. Dimercurated products were obtained at higher temperatures, especially if an excess of the acetate were present. In the case of  $\beta$ -naphthylurea the di-derivative separated mixed with the mono-derivative, whereas only the mono-derivative was obtained from  $\alpha$ -naphthylurea. None of the mercurated products seem to have been described before. The corresponding mercurated thioureas decomposed, as stated above, yielding black HgS slowly, and could not therefore be properly used.

The mercury in the products was estimated by the "Gold crucible method" (cf. Whitmore, "Organic Derivatives of Mercury", p. 355) and the nitrogen by Kjeldahl's method.

The bactericidal action against a 24 hours' culture in nutrient peptone-broth of *B. Coli* was studied by the Rideal-Walker Drop method as in Part I (*loc. cit.*).

The following table gives a summary of the bactericidal data.

TABLE I

Organism: *B. Coli*. Period of incubation = 48 hours at 36°.

Substituent.	Ureas	Maximum effective dilutions of	
		Thioureas.	Mercurated ureas.
Phenyl	1:300	1:400	1:120,000
<i>o</i> -Tolyl	1:300	1:300	1:100,000
<i>m</i> -Tolyl	1:400	1:300	1:100,000
<i>p</i> -Tolyl	1:400	1:400	1:80,000
<i>o</i> -Chlorophenyl	1:300	1:400	1:140,000
<i>m</i> -Chlorophenyl	1:300	1:400	1:120,000
<i>p</i> -Chlorophenyl	1:500	1:300	1:140,000
$\beta$ -Naphthyl	1:400	1:500	1:140,000
$\alpha$ -Naphthyl	1:600	1:500	1:160,000
<i>o</i> -Carboxyphenyl		1:500	...
<i>m</i> -Carboxyphenyl	1:400	1:400	1:19,000
<i>p</i> -Carboxyphenyl	1:500	1:500	1:20,000
<i>m</i> -Nitrophenyl	1:200	..	1:80,000

## EXPERIMENTAL

As has already been mentioned, the phenyl-, tolyl-, naphthyl- and *m*-nitrophenyl-ureas were prepared and purified by known methods (Davis and Blanchard, "Organic Syntheses", Vol. 1, p 453; Weith, *Ber.*, 1878, 9, 220) The chlorophenylureas separated at first as oils which solidified on keeping in a refrigerator for several hours; after which they were powdered, filtered and washed with dilute acetic acid before recrystallisation from hot water or hot dilute alcohol.

While phenyl-, tolyl- and *m*-nitrophenyl-ureas gave monomercurated products by mercuration with equimolecular quantity of mercuric acetate in dilute acetic acid at the ordinary temperature,  $\beta$ -naphthylurea gave a mixture of mono- and di-mercured products. The latter being less soluble separated first and were recrystallised from glacial acetic acid. In case of the  $\alpha$ -naphthylurea only the di-derivative was obtained.

The position of the acetoxymercuri group was assumed to be *para* to the urea group in the mono-derivatives.

The carboxyphenylureas were prepared as follows. *m*-(or *p*)-Aminobenzoic acid (13.7g., 1 mol.) was first dissolved in hot water (30 c.c.). To this was added slowly 8.1 g. of KCNO (1 mol.) in water (100 c.c.) and the mixture heated at 100° for 3½ hours. The cooled mixture was filtered and washed with water. The residue was then dissolved in dilute sodium hydroxide and precipitated by dilute acetic acid. They were recrystallised from hot water or hot alcohol. In the case of anthranilic acid the mixture was heated at 100° for 4 hours and then evaporated to dryness on a water-



bath. The residue was washed with warm water, dissolved in dilute NaOH and reprecipitated with dilute acetic acid. The yield was poor. The mercury derivative could not be obtained pure.

The urea derivatives were mercurated in the usual way and obtained as white amorphous powders, easily soluble in dilute NaOH and insoluble in organic solvents excepting hot acetic acid.

The phenyl-, tolyl- and chlorophenyl-thioureas were prepared through the corresponding mustard oils (Davis and Blanchard, "Organic Syntheses", Vol. I, p. 437). The naphthyl derivatives were obtained by the action of ammonium thiocyanate on the hydrochloride of the bases (Declermont, *J. Chem. Soc.* 1877, 1, 79). The carboxyphenyl derivatives, which are new, were prepared in the same way in good yield. On mercuration only the di-mercuri derivatives were obtained with phenyl- and tolythioureas but mono-derivatives in case of the carboxyphenylthioureas.

Table II gives the names, melting points or decomposition temperatures and the analytical data of the phenylureas and thioureas, and Table III gives the decomposition temperatures and percentage of mercury in the mercuri derivatives.

TABLE II

Compounds.	M.p.	% Nitrogen	
		Found.	Calc.
<i>o</i> -Carboxyphenylurea	294°	15.38	15.5
<i>m</i> -Carboxyphenylurea	265°	15.43	15.5
<i>p</i> -Carboxyphenylurea	Does not melt, softens at 180°, finally solidifies.	15.32	15.5
<i>o</i> -Carboxyphenylthiourea	181°	14.44	14.28
<i>m</i> -Carboxyphenylthiourea	185°	13.98	14.28
<i>p</i> -Carboxyphenylthiourea	194°	13.96	14.28

TABLE III

Compounds.	Decomp temp	% Mercury	
		Found.	Calc.
Acetoxymercuri-phenylurea	125°	50.9	50.8
„ <i>o</i> -tolylurea	200°	48.86	49.09
„ <i>m</i> -tolylurea	215°	49.18	49.09
„ <i>p</i> -tolylurea	238°	43.83	49.09
„ <i>o</i> -chlorophenylurea	158°	46.61	46.7
„ <i>m</i> -chlorophenylurea	163°	46.82	46.7
„ <i>p</i> -chlorophenylurea	172°	46.59	46.7
„ (mono) $\beta$ -naphthylurea	182°	45.18	45.1
„ (di) $\beta$ -naphthylurea	284°	57.29	57.02
Diacetoxymercuri- $\alpha$ -naphthylurea	210°	57.17	57.02
Acetoxymercuri- <i>m</i> nitrophenylurea	202°	45.49	45.6
„ <i>m</i> -carboxyphenylurea	256°	45.54	45.7
„ <i>p</i> -carboxyphenylurea	270°	45.58	45.7
„ -phenylthiourea		59.62	59.9
„ <i>o</i> -tolylthiourea		58.59	58.72
„ <i>m</i> -tolylthiourea		58.62	58.72
„ <i>p</i> -tolylthiourea		58.65	58.72

In order to test the stabilities of the mercurated phenylureas, 5 representative members, viz. (1) phenyl, (2) *p*-chlorophenyl, (3) *p*-tolyl, (4)  $\alpha$ -naphthyl and (5)  $\beta$ -naphthyl derivatives, were shaken at room temperature (about 35°) with the following reagents: (a) *N*-HCl, (b) *N*-KI, (c) *N*-(NH<sub>4</sub>)<sub>2</sub>S and (d) a dilute hydrazine sulphate solution containing KOH, for about one hour.

Mixture (d) produced reduction to black mercurous oxide with (3) and (4) most rapidly and less so with (5) and (2); (1) being the least easily attacked. Reagent (a) after one hour liberated ionised mercury very slowly with (2) and (5), the filtrate giving pale yellow colour with H<sub>2</sub>S solution; but very indistinctly with others. Reagent (b) liberated small amounts of potassium acetate after one hour, as tested with FeCl<sub>3</sub> added to the filtrate, compound (4) giving the deepest colour. Reagent (c) had very slight effect even after one hour, giving faint yellow colour with (3), (4) and (5) but not with (1) and (2). On the whole the compounds may be regarded as being reasonably stable, except to the action of the powerful reducing agent, hydrazine hydrate.

The mercurated ureas were generally formed in good yield and were stable in air or in light and in hot aqueous and alcoholic solution; the naphthyl derivatives, however, turned slightly grey on long exposure to light. They were not decomposed by dilute NaOH (no liberation of HgO) but were slowly decomposed by continued passage of hydrogen sulphide through their warm solution in dilute acids. The introduction of mercury remarkably increased the activity of the urea derivatives. The *p*-chloro derivative and the  $\beta$  naphthyl derivative (both active in 1:140,000) and the  $\alpha$ -naphthyl derivative (active in 1:160,000), appear to be quite satisfactory. They may possibly be used with advantage in paper, glue and leather industries.

CHEMICAL LABORATORY,  
RAVENSHAW COLLEGE,  
CUTTACK 3, ORISSA.

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## STUDIES ON RANCIDITY OF BUTTERFAT. PART II. THE USE OF L-ASCORBYL ESTERS OF FATTY ACIDS AS ANTIOXIDANTS

BY S. MUKHERJEE, S. RAY AND M. GOSWAMI

A method for the preparation of *l*-ascorbyl esters of fatty acids in good yield is described. The antioxidant activity of these esters have been tested with butterfat both by storage experiments and by Swift's stability test. The biological availability of these esters has also been tested by carrying out assay with guinea-pigs. The loss of *l*-ascorbyl esters within the induction period has been determined.

In a previous paper (Mukherjee and Goswami, this *Journal*, 1947, **24**, 239) of this series it has been shown that *l*-ascorbic acid possesses good antioxidant properties, particularly when used in combination with other antioxidants, but its use in the case of fat is limited because of its insolubility in the same. The fact that esters of *l*-ascorbic acid with fatty acids like stearic, palmitic etc. are quite soluble in fat, makes its incorporation much easier, in such forms. Hence, attempts were made to prepare the respective *l*-ascorbyl esters of the following fatty acids: stearic, palmitic, myristic and lauric. The method originally employed by Swearn, Sterton, Turner and Wells (*Oil & Soap*, 1943, **20**, 224) was found to give very low yields and in most cases the esters could not be prepared using a 16-hour reaction time employed by them. A detailed study regarding proportions of the reactants, time of reaction, effect of mechanical agitation and temperature has finally led to a successful preparation of these esters in quantity. The method employed is outlined briefly as follows.

### EXPERIMENTAL

About 25 g. of the finely powdered fatty acid was added to 250 c.c. of concentrated  $H_2SO_4$  containing 30.0 g. of *l*-ascorbic acid in solution at  $30^\circ$  with thorough stirring till the solution became clear; it was necessary to cool the mixture externally during the reaction. The reaction mixture was then shaken for 96 hours at room temperatures ( $34^\circ$ - $37^\circ$ ) in a mechanical shaker. During this period the whole solution became dark coloured. The solution was then slowly added to about 500 g. of crushed ice with thorough stirring till the oily liquid solidified. The mixture was then allowed to attain room temperature and extracted with ether, ethereal layer washed free from sulphuric acid, dried over anhydrous  $Na_2SO_4$ , and ether distilled off; the residual solid obtained was purified by repeated recrystallisation according to Swearn *et al.* (*loc. cit.*) except that the treatment with charcoal was found necessary to obtain a perfectly white crystalline product. The melting points of the esters, when dried in a vacuum desiccator over  $P_2O_5$ , however, were found to be identical with those reported by Swearn *et al.* (*loc. cit.*). The yield of the purified ester varied from 50-60%.

The effect of these four esters on the retardation of rancidity of butterfat was determined both by the Swift fat stability test (King, Roschen and Irwin, *Oil & Soap*, 1933, 10, 105) and by storage experiments. Table I records the results obtained with the first method, the end of the induction period being taken as the time necessary to reach a peroxide value of 10.0

TABLE I

*Antioxidant activity of fatty acid esters of l-ascorbic acid on butterfat (Swift stability test) at 100°.*

	Antioxidant.	Conc.	Induction period	Protection factor.
1	L-Ascorbyl stearate	0.01%	45 hrs.	1.25
2	„ palmitate	0.01	48	1.40
3	„ myristate	0.01	50	1.50
4	„ laurate	0.01	52	1.60
5	Control	—	20	—

It appears from Table I that the esters lengthen the induction period to some extent. But it should be borne in mind that these fatty acid esters of l-ascorbic acid are very much liable to oxidation, particularly under the drastic conditions which are employed in the Swift stability test. So, from the positive values of the protection factor obtained above, it can safely be expected that the degree of protection will be much higher with actual storage experiments the results of which are detailed below.

TABLE II

*Antioxidant activity of fatty acid esters of l-ascorbic acid on butterfat on storage at 37°.*

Antioxidant.	Conc.	Peroxide value after days at 37°.						
		0.	15	30.	45.	60	90.	120.
1. L-Ascorbyl stearate	0.01%	0.0	0.0	0.02	0.10	0.2	1.16	5.74
2. „ palmitate	0.01	„	„	0.02	0.10	0.2	1.0	4.83
3. „ myristate	0.01	„	„	0.03	0.13	0.2	1.2	5.9
4. „ laurate	0.01	„	„	0.02	0.15	0.25	1.3	4.63
5. Control	—	„	0.15	0.40	2.8	14.2	29.2	90.1

The results in Table II clearly indicate the marked protection of these four ascorbyl esters of fatty acids on the storage of butterfat at 37° and as such, should find practical

application. The vitamin activities of these esters were checked by biological assay as detailed below.

*Biological Availability of l-Ascorbyl Esters of Fatty Acids.*—As the structure to which the antiscorbutic action of *l*-ascorbic acid is attributed might presumably have remained unchanged in these esters, it would be reasonable to believe that these fatty acid esters of *l*-ascorbic acid will also possess such activity. The object of the present work is to see how far this activity has been retained (or destroyed) in these esters. This can best be tested by determining the biological availability by subjecting them to biological assay with guinea-pigs.

Normal and healthy male guinea-pigs (av. bodyweight, 250-300 g.) were divided into 5 different groups; they were maintained on the following scorbutic diet consisting of crushed barley (64 parts), crushed gram (20 parts), casein (12 parts), cod liver oil (2 c.c.) and water to drink *ad lib*. When the animals just began to show a steep fall in body-weight (after 20-23 days) the first group of animals was given 0.5 mg. of synthetic *l*-ascorbic acid per animal. The 2nd, 3rd and 4th groups of animals were given an amount of the different esters containing 0.5 mg. equivalent of indophenol-reducing substance as a supplement to the above basal diet. The fifth group was used as a control to which no supplement was added to the scorbutic diet. The supplement was continued for two weeks when the animals showed steady and proportionate increase in body-weight. The results of the biological assay are shown in Table III below and graphically in Fig. 1.

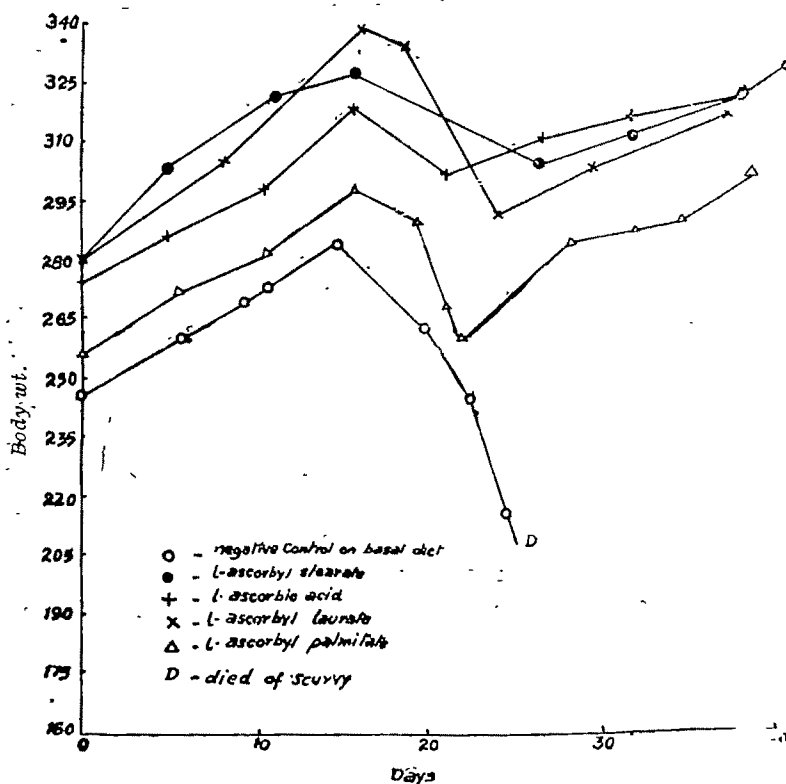
TABLE III

Group.	Daily supplement.	No. of guinea-pigs.	Average wt. on the day on which supplements started.	Average wt after two weeks of supplement.	Average gain.
1	<i>l</i> -Ascorbic acid	2	296 g.	323 g.	+27 g.
2	<i>l</i> -Ascorbyl laurate	3	287	315	+28
3	„ palmitate	3	258	286.5	+28.5
4	„ stearate	3	310	335	+25
5	No supplement to basal diet	2	—	Died of scurvy	

These results clearly indicate that the ascorbyl esters possess antiscorbutic activity comparable to equivalent amounts of *l*-ascorbic acid. Hence, the use of such esters as antioxidants for fats provide a method for incorporation of vitamin-C in fats and oils. The biological utilisation of the fatty acid mono-esters of *l*-ascorbic acid being comparable to that of ascorbic acid itself, it would be advantageous in certain vitamin preparations to use this fat-soluble form of vitamin-C.

Of the esters tested *l*-ascorbyl palmitate was found to have the greatest activity, nearly 2.35 mg. of the esters being equivalent to 1 mg. of *l*-ascorbic acid.

FIG. 1



*Antioxidant Losses during the Induction Period of Fat Oxidation.*—It has been known for long that the part played by antioxidants in stabilising oils and fats is primarily to retard the oxidation of the unsaturated glycerides by inhibiting the normal chain of oxidation reactions that would have taken place in absence of the added antioxidants, these substances instead are themselves oxidised. It is expected therefore that the concentration of the effective antioxidant should show a decrease during the induction period of fats, and it seems desirable to determine to what extent such antioxidants, as *l*-ascorbyl esters of fatty acids, would be affected, for this will enable us to know the exact picture when such esters are actually incorporated in fats for stabilisation and fortification as well. For this purpose the loss of the *l*-ascorbyl esters during development of rancidity in butterfat was determined progressively. The antioxidants were added in two different concentrations of 0.05% and 0.02% in the butterfat and the samples oxidised at 37° by drawing in a slow current of purified and dried air through them at a constant rate. Samples were drawn out every 24 hours and determination of the peroxide content and *l*-ascorbyl esters was made, using a modified Wheeler method in the first case (Wheeler and Pascheek, *Oil & Soap*, 1944, 21, 33) and in the second, that of Turner and Speck (*Ind. Eng. Chem. Anal. Ed.*, 1944, 16, 464) using a standard solution of the sodium salt of 2:6-dichlorophenol-indophenol in dry acetone. The results are tabulated below.

TABLE IV

*Disappearance of antioxidants during oxidation of butterfat at 37°.*

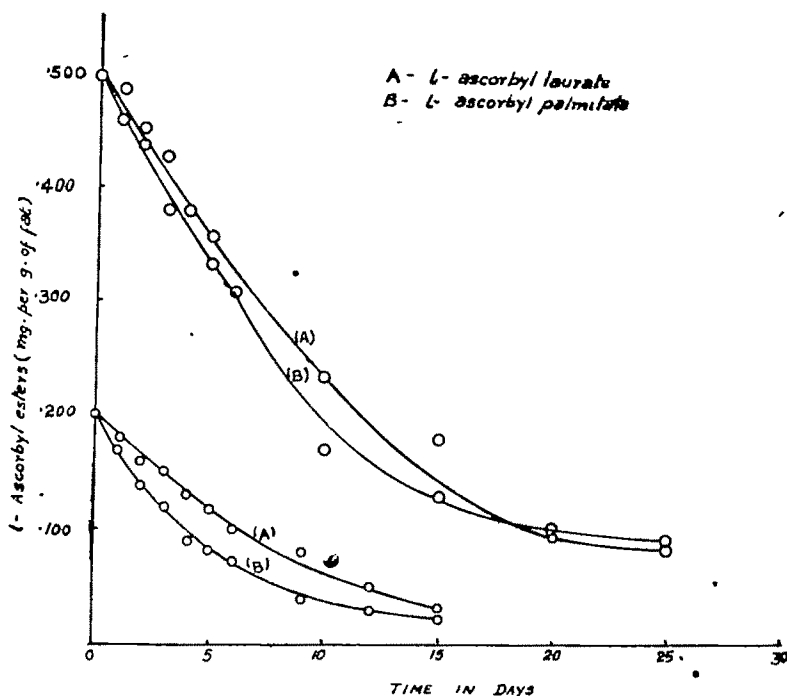
		A. Peroxide value after days.									
	Antioxidants.	Initial conc.	1.	2.	3.	5.	6	8	10.	15.	20.
1	<i>l</i> -Ascorbyl palmitate	0.05%	0.0	0.1	0.5	1.0	1.5	2.6	4.3	7.0	10.2
2	" "	0.02	0.0	0.1	0.6	1.2	1.6	2.8	5.0	8.1	11.6
3	" laurate	0.05	0.0	0.14	0.4	0.9	1.2	2.0	4.0	7.0	10.2
4	" "	0.02	0.0	0.15	0.45	1.0	1.6	2.4	4.0	7.7	10.8
5	Control	—	0.2	0.8	1.2	4.0	6.75	8.6	16.5	18.2	20.3

B. *l*-Ascorbyl esters in mg./g. of fat after days.

		1.	2.	3	4.	5.	6.	9.	10.	12.	15	20	25.
1. <i>l</i> -Ascorbyl palmitate	0.05%	0.49	0.45	0.43	0.38	0.36	3.32	—	0.24	—	0.10	0.095	0.085
2. Do	0.02	.18	.16	.15	.13	.12	.10	.08	.05	.05	0.3	—	—
3. <i>l</i> -Ascorbyl laurate	0.05	.46	.44	.38	—	.33	.31	—	.17	—	.13	.10	.09
4. Do	0.02	.17	.14	.12	.09	.08	.07	.04	—	.03	.02	—	—

Figure 2 represents the rate of disappearance of *l*-ascorbyl palmitate and laurate during the accelerated oxidation of butterfat at 37°. From Table IV the loss of *l*-ascorbyl esters during autoxidation appears to proceed at first fairly rapidly and then slowly within the induction period, but even after the induction period is over the whole of the ascorbyl esters are not destroyed. Moreover, a sharp rise in the peroxide concentration never occurs until more than half of the ascorbyl esters is destroyed, e g., after 10 days of blowing.

FIG. 2

*Rate of disappearance l-ascorbyl esters during oxidation at 37°.*

The present study on the antioxidant behaviour of *l*-ascorbyl esters of fatty acids with butterfat reveals that in actual storage experiments, these esters retard the onset of rancidity to the extent that the induction period of the fat is more than doubled. These fat-soluble esters of ascorbic acid retain their antiscorbutic action and hence, when added as antioxidants, may serve as a source of additional vitamin. The loss of *l*-ascorbyl laurate and palmitate within the induction period has been determined, but it has been found that even when the induction period is over, the ester is not completely oxidised. A suitable method for the preparation of the various esters in suitable yield has been presented.

DEPARTMENT OF APPLIED CHEMISTRY,  
UNIVERSITY COLLEGE OF SCIENCE  
CALCUTTA.

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# STUDIES ON RANCIDITY OF BUTTERFAT. PART III. USE OF ETHYL GALLATE IN COMBINATION WITH OTHER ANTIOXIDANTS

By S. MUKHERJEE, S. RAY AND M. GOSWAMI

Ethyl gallate in combination with *l*-ascorbyl esters of fatty acids as well as hydrogen gas possesses a very strong antioxidant activity. Destruction of carotene and vitamin-A within the induction period is not appreciable but beyond it they are readily destroyed; the various antioxidants tried afford only very slight protection beyond the induction period.

The marked antioxidant activity of ethyl gallate has already been observed by Lea (*J. Soc. Chem. Ind.*, 1944, **63**, 107). The activity of this substance was also determined with the Swift stability test and the protection factor obtained with butterfat, when used in concentration of 0.005%, was found to be 8.0. In view of the pronounced activity of ethyl gallate, as also of the ascorbyl esters, and the observed behaviour of hydrogen by the present authors (Mukherjee and Goswami, this *Journal*, 1947, **24**, 239) it was considered necessary to try the various combinations using these substances. The results of storage experiments are shown in Table I.

TABLE I  
*Antioxidant activity with butterfat at 37°.*

	Peroxide value after days.					
	15.	30.	45.	60.	90.	120.
1. Control	0.15	0.40	2.8	14.5	31.2	102.0
2. Hydrogen (passed for 2 hours at 50°)	0	0	0.02	0.20	1.0	1.2
3. Ethyl gallate (0.005%)	0	0	0.01	0.16	1.0	1.0
4. Ethyl gallate+hydrogen at 50° for 2 hrs.	0	0	0.01	0.08	0.75	0.70
5. Ethyl gallate+ascorbyl palmitate (0.01%)	0	0	0.01	0.10	0.80	1.0
6. Ethyl gallate+ascorbyl palmitate+ hydrogen at 50° for 2 hrs.	0	0	0.0	0.05	0.40	0.52

From these results it seems that quite desirable results can be observed when suitable combinations are used and the results of these experiments can successfully be utilised commercially. The results of storage experiments in large sealed tins (5 lbs.) for a period of five months are shown below, which definitely indicate the commercial possibilities.

TABLE II

Storage conditions. Package	Antioxidant.	Peroxide value after 5 months.
1. Hydrogen	—	1.8
2. Hydrogen	Ethyl gallate (0.005%)	1.0
3. Hydrogen	Do +ascorbyl palmitate (0.01%)	1.0

*Protective Effect of the Added Antioxidants on the Destruction of Carotene  
and Vitamin-A in the Oxidation of Butterfat*

It has been observed in course of rancidity studies with butterfat (cow) that the yellow colour of the fat is completely bleached on ageing. In this section studies have been made with a view to giving an idea as regards its connection with the development of rancidity in fats and also the rate of destruction of vitamin-A in the butterfat. It is a common observation that fairly old samples of butterfat give negative Carr-Price test. Certain studies have been carried out by Lovern (*J. Soc. Chem. Ind.*, 1944, 68, '67) in this connection regarding the destruction of vitamin-A in halibut liver oil. Since the vitamin-A content of butterfat is very low, the studies were conducted with samples of butterfat fortified with synthetic vitamin-A in the form of acetate. The rate of deterioration was followed at 40° by blowing air through the molten fat samples, by the determination of peroxide value, and the total amount of carotene and vitamin-A was measured with the help of Lumetron photo-electric colorimeter, using ultraviolet light in the second case and with the proper combination of filters. The experimental results are shown in Table III.

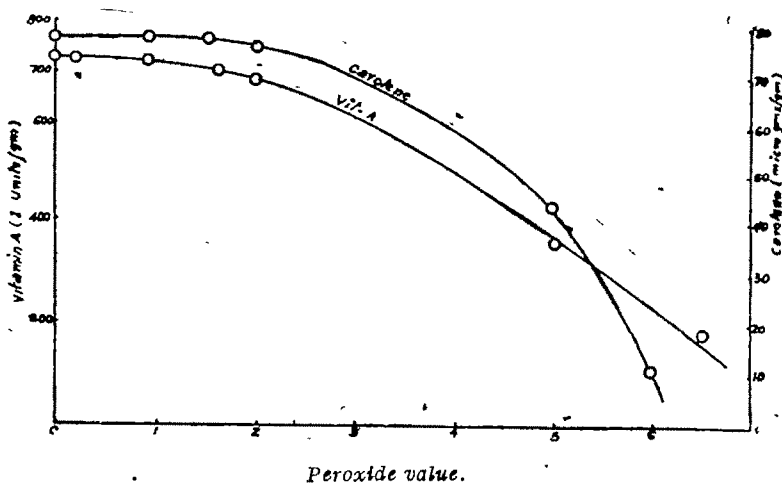
TABLE III

*Peroxide value and destruction of carotene & vitamin-A at 38.5°.*

Days of blowing.	Peroxide value.	Carotene (micro g. per 100 g.)	Vitamin-A (I.N.U./g.)	Peroxide value.	Carotene (micro g. per 100 g.)	Vitamin-A (I.N.U./g.)
Control sample.				With ethyl gallate (0.005%).		
0	0.0	76.8	725	0.0	76.8	725
1	0.84	76.5	710	0.24	76.8	718
2	1.50	75.9	695	0.84	76.6	715
3	2.20	75.6	680	1.20	76.3	710
4	5.75	43.2	350	1.80	76.0	697
5	6.50	10.0	187	2.20	64.9	675
6	9.4	0.0	120	2.9	58.8	500
7	13.1	0.0	88	6.2	45.0	317
8	18.2	0.0	37.5	8.4	30.2	282
With ascorbyl palmitate (0.01%).				With ascorbyl palmitate (0.01%) + $\alpha$ -tocopherol (0.005%).		
	0.0	76.8	725	0.0	76.8	725
1	0.25	76.8	715	0.20	76.8	715
2	0.95	76.5	710	0.68	76.6	712
3	1.44	76.0	700	1.00	76.3	710
4	1.76	75.5	688	1.50	76.0	700
5	2.58	75.0	641	1.85	75.7	675
6	4.43	55.4	450	2.40	72.0	600
7	7.0	40.0	335	4.40	58.0	446
8	9.0	25.0	251	6.5	44.0	392

The results of experiments carried out with these antioxidants tend to show that the conservation of vitamin-A and carotene in ghee can very well be achieved by addition of suitable antioxidants. Most pronounced effect has been observed with a mixture of  $\alpha$ -tocopherol and ascorbyl palmitate. Ethyl gallate affords a marked protection in as low a concentration as 0.005%. The development of peroxide value and the rate of destruction of carotene and vitamin-A are shown graphically with the control sample in Fig. 1. The results in the table tend to show that the

FIG. 1



loss of carotene or vitamin-A is not appreciable unless a certain peroxide level is attained by the fat, and it may very well be said that during the induction period of the fat, these substances undergo very little changes. Once the induction period is past and rapid oxidation sets in, the vitamin-A and carotene are very rapidly destroyed but still then the antioxidants afford a certain degree of protection outside the induction period.

## ENOL CONTENT OF 2-FORMYL KETONES (HYDROXYMETHYLENE KETONES). PART II

BY MISHRI MAL BOKADIA AND S. S. DESHPANDE

Enol contents of some more hydroxymethylene ketones have been estimated by the methods of K. H. Meyer and Hibber and a difference between the two results, as reported previously, has again been observed. Enols have also been estimated by titration against *N*/5 caustic soda solution at  $-10^{\circ}$  and the values obtained are found to be in agreement with those obtained by Meyer's method.

In Part I (this *Journal*, 1949, 26, 455) the enol contents of five hydroxymethylene ketones were reported and it was shown that the enol contents determined by K. H. Meyer's method (*Ber.*, 1911, 44, 2718) were generally higher than those obtained by Hibber's copper acetate method (*Ber.*, 1921, 54, 902). We have extended the work and have determined enol contents of (1) hydroxymethylene menthone, (2) hydroxymethylene cyclopentanone, (3) hydroxymethylene bromoethyl acetate and hydroxymethylene bromoacetone by both these methods. We have confirmed our previous observation that the values for enol content obtained by K. H. Meyer's method are in each case higher than those obtained by Hibber's method. These results are shown in Table I.

In regard to the stages constituting K. H. Meyer's bromine process, evidence about the formation of dibromo addition product of enol and of the formation of the corresponding bromoketone by loss of hydrobromic acid from it, which constitute the first and the second stage respectively of the process, was shown in a paper by one of us (S. S. D.) (this *Journal*, 1946, 23, 43). The third stage in the process is the reduction of bromoketone to the parent ketone by acidified potassium iodide with the liberation of two atoms of iodine per molecule of the enol. This stage has now been examined by us. By means of acidified potassium iodide we reduced some bromo- $\beta$ -ketonic esters, two bromohydroxymethylene ketones, and two simple  $\alpha$ -bromoketones. The iodine liberated was found in each case to be about equal to the calculated value, namely two atoms of iodine per molecule of the bromo compound. These results are shown in Table II of the experimental part. Thus, the mechanism postulated by K. H. Meyer in his process of estimating enol has been critically examined and verified.

That the parent hydroxymethylene ketone was actually formed by the action of acidified potassium iodide on the bromoketone, produced at an intermediate stage in the Meyer's process, was demonstrated by starting with hydroxymethylene cyclopentanone, which is a solid. On treatment with bromine, followed by addition of acidified potassium iodide, iodine was liberated which was titrated against sodium thiosulphate. On extracting with ether the liquid left after titration and on removal of its solvent, the residue was identified to be hydroxymethylene cyclopentanone.

The discrepancy about the results of enol content obtained by the methods of Meyer and Hibber, however, could not be explained.

A method for estimating enol in a keto-enol equilibrium mixture has been suggested by Seidel *et al.* (*Ber.*, 1936, 69, 650) who titrated an absolute alcoholic solution of the mixture at  $-10^{\circ}$  with  $N/5$  caustic soda solution. The authors have shown that under these conditions the values of enol obtained are in close agreement with those obtained by K. H. Meyer's method. We used the titration method in the case of some hydroxymethylene ketones and found that here too there is a good agreement between the results obtained by the titration method and Meyer's method. These results are shown in Table III.

### EXPERIMENTAL

The estimations of the enol contents by Meyer's method and Hibber's method were carried out exactly in the same way as described in Part I (*loc. cit.*). The results obtained are given below.

TABLE I

Hydroxymethylene ketones.	Percentage of enol by Meyer's method.	Hibber's method.	Reference
1 Hydroxymethylene cyclopentanone	99.3%	47.87%	Wallach <i>et al.</i> , <i>Annalen</i> , 1923, 329, 114.
2 Hydroxymethylene menthone	74.0	20.0	Bishop, Claisen and Sinclair, <i>Annalen</i> , 1894, 281, 394.
3 Hydroxymethylene bromoacetone	55.58	15.32	Mahala & Deshapande (unpublished work)
4 Hydroxymethylene bromoethyl acetate	78.6	...	Gupta & Deshapande (unpublished work)

*Reduction of Bromoketonic Systems.*—Weighed amounts of bromoketones were dissolved in absolute alcohol and treated with acidified potassium iodide and slightly warmed. The iodine liberated was titrated against standard sodium thiosulphate solution. The results obtained are given in Table II.

TABLE II

Bromo compounds.				Amount of iodine liberated by 1 gram mol. of bromoketone.	Mols. of iodine
1 $\alpha$ -Bromoethyl acetoacetate	...	...	...	252.5 g.	0.99 mol.
2 $\gamma$ -Bromoethyl acetoacetate	...	...	...	257.4	1.01
3 $\alpha\alpha$ -Dibromoethyl acetoacetate	...	..	...	499.2	1.96
4 Hydroxymethylene bromoacetone	...	...	...	249.5	0.98
5 Hydroxymethylene bromoacetophenone	...	...	...	253.0	0.99
6 2-Bromoacetone	...	...	...	254.1	1.00
7 $\omega$ -Bromoacetophenone	...	...	...	254.0	1.00

*Recovery of the Parent Compound from the Reduction Product.*—To absolute alcoholic solution of hydroxymethylene cyclopentanone alcoholic solution of bromine was

added in slight excess at room temperature until a faint red colour persisted. On adding a strong aqueous solution of potassium iodide, followed by 2 c.c. of dilute sulphuric acid, iodine was liberated which was removed by adding aqueous sodium thiosulphate. On extracting the solution with ether and on removal of the solvent, a solid residue was left which on purification by crystallisation melted at  $73^{\circ}$ , and was thus identified as hydroxymethylene cyclopentanone.

*Enol Content by Caustic Soda Titration Method.*—Dittmer (Ber., 1936, 69, 650) carried out the titrations of keto enol mixtures at room temperature. Several experiments were performed by us at various temperatures and the following method was found to give reliable results.

A weighed amount of the substance was dissolved in absolute alcohol and cooled to  $-10^{\circ}$ . This was titrated against  $N/5$  aqueous caustic soda solution using phenolphthalein as an indicator. The results obtained are given in Table III.

TABLE III

Hydroxymethylene ketones.		Percentage of enol by		
		NaOH method	Meyer's method.	Hibber's method
1.	Hydroxymethylene methylethyl ketone ...	96.0%	96.0%	64.1%
2.	„ diethyl ketone ...	98.97	*97.0	35.5
3	„ desoxybenzoin ...	90.0	90.2	89.7
4.	„ cyclohexanone ...	73	72.5	74.5
5.	„ cyclopentanone ...	99.0	99.3	47.87
6.	„ menthone ...	74.0	74.5	20.0

\* The value of the enol content reported in Part I was 57%. The compound then prepared was liquid and was purified by distillation. We prepared the compound now in winter and obtained it as a solid (m.p.  $40^{\circ}$ ). The enol estimation was done with the solid compound this time.

CHEMICAL LABORATORIES,  
AGRA COLLEGE, AGRA.

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## ON THE NATURE OF LEAD-ACETATO COMPLEX ION AND THE LEAD ACETATE MOLECULE

BY KUMAR KRISHNA CHATTERJI

The formation of the cationic complex  $\text{PbAc}^+$  ion has been studied by measurements of the lowering of freezing point of the system eutectic  $\text{KNO}_3\text{-H}_2\text{O}$ , by mixtures of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{KAc}$  solutions

By the same method it has been shown that the complex  $\text{PbAc}^+$  and  $\text{Ac}^-$  ions are produced by the primary dissociation of lead acetate molecule in solution.

The formation of a lead-acetato complex ion by the reaction between a lead salt and an alkali or ammonium acetate in solution has been established through the work of Edmonds and Birnbrown (*J. Amer. Chem. Soc.*, 1940, **62**, 2367) and Purkayastha and Sen Sarma (this *Journal*, 1946, **23**, 39), the former workers employing solubility measurements and the latter, from thermometric and conductometric titrations

Although the methods of study applied by Purkayastha and Sen Sarma appear more accurate than their foregoing workers, the Job's method of continued variation employed by them to obtain the value of the instability constant of the complex ion is subject to criticism in the present case.

A constant value for instability constant can also be obtained if a two-fold condensed ion  $[\text{Pb}_2\text{Ac}_2]^{++}$  is assumed in place of a single ion  $[\text{PbAc}]^+$  as advocated by previous workers.

Such an assumption is supported by the fact that one of the lead-acetato perchlorates, isolated by Weinland and Stroch (*Ber.* 1922, **55**, 553, 2706) has been formulated as a two-fold condensed complex  $[\text{Pb}_2\text{Ac}_2][\text{ClO}_4]_2\text{-H}_2\text{O}$  from the measurement of its conductivity in solution.

Besides, a large number of inorganic molecules, formerly regarded as simple molecules, have been shown by physico-chemical measurements during recent years to exist in polymerised state in solution.

From these considerations it appears that in the absence of some direct evidence, the nature of the lead-acetato complex ion is still unsettled and calculation of its dissociation constant by the foregoing workers is based on a somewhat arbitrary assumption that a simple  $[\text{PbAc}]^+$  ion is formed.

The present author has followed the reaction between lead nitrate and potassium acetate in solution from measurements of the depression of freezing points of the eutectic  $\text{KNO}_3\text{-H}_2\text{O}$  ( $2.87^\circ$ ). The method is based on the observation of Lowenharz (*Z. physikal. Chem.*, 1895, **18**, 70) that the cryoscopic rule of Raoult is applicable to the case of (1) transition point of a salt hydrate, (2) melting point of the salt hydrate and (3) the eutectics, and was first employed by Darmon (*Bull. Soc. Chim. Belg.*, 1927, **36**, 64) and later by Cornec and Muller (*Compt. rend.*, 1932, **194**, 1735), and particularly by Souhey (*Bull. soc. chim.*, 1946, **v**, **13**, 160) during recent years for determining the state of aggregation of a large number of inorganic ions in solution.

The lowering of freezing point is connected with the concentration of the dissolved solute by the simple equation  $\Delta t = K.C$ , where  $\Delta t$  = lowering of freezing point,  $C$  = concentration in g. moles of the dissolved substance or ion and  $K$  = molecular lowering constant = 1.7 for a single ion or an undissociated molecule.

The present method of study has been employed because of its having the following advantages over the classical cryoscopic method :

(1) The value of the molecular lowering changes very slightly with changes of concentration  $C$  of the dissolved substance, as the ionic force of the medium is primarily due to the ions of the salt hydrate and the addition of small quantities of the substance, molecular lowering of which is to be measured, changes the ionic force very little.

(2) The lowering of freezing point of the eutectic  $\text{KNO}_3\text{--H}_2\text{O}$  is independent of the presence of  $\text{K}^+$  and  $\text{NO}_3^-$  ions liberated by the dissolved potassium acetate and lead nitrate, and only the complex ion formed and its dissociation products will exert any influence in depressing the freezing point of the eutectic.

Freezing point measurements in the above system by mixing together lead nitrate and potassium acetate in different proportions indicate that a complex lead acetate ion is formed by interaction between these substances, in which the lead and acetate ions are in the ratio 1:1.

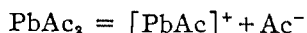
Comparison of the theoretical values of depression of the freezing point calculated from the values of the instability constant  $K$  of the  $[\text{PbAc}]^+$  ion obtained by the foregoing workers and from the value of  $K$ , calculated by the author on the assumption of a two-fold condensed ion  $[\text{Pb}_2\text{Ac}_2]^{++}$ , have been made with the experimental value.

It has been found that the experimental value of the lowering closely agrees with the theoretical value calculated from the value of  $K$  obtained by Edmonds and Birnbow and is somewhat smaller than that calculated from the data of Purkayastha and Sen Sarma. The result shows that the complex ion is  $\text{PbAc}^+$  ion, as has been assumed by the foregoing workers.

The low value of the degree of dissociation of the lead acetate molecule, obtained from conductivity measurements, was explained by Sandved (*J. Chem. Soc.*, 1927; 1967), that the  $[\text{PbAc}]^+$  ion is probably formed by primary dissociation of the lead acetate molecule.

The present author has adduced direct evidence in this respect from measurement of the lowering of freezing point of the system eutectic  $\text{KNO}_3\text{--H}_2\text{O}$  by lead acetate. It has been found that at different concentrations of lead acetate, the depression corresponds to the formation of two ions only in solution, from dissociation of the lead acetate molecule.

The simplest way of interpreting these results is to assume that the lead acetate behaves in solution mainly as a binary electrolyte dissociating into  $\text{PbAc}^+$  and  $\text{Ac}^-$  ions in solution according to the equation,



the secondary dissociation of the lead-acetato ion formed is practically so negligible that the lead acetate molecule may be looked upon as a complex acetato-acetate of lead.



## EXPERIMENTAL

Merck's lead nitrate, potassium nitrate, potassium acetate and lead acetate of analytical reagent quality have been used in all the measurements.

The freezing point measurements were carried out in the Beckmann's apparatus commonly used in the laboratories. The cooling bath was provided by a mixture of crushed ice and common salt, the temperature at equilibrium not falling below  $10^{\circ}$ .

In Table I and Fig. 1 have been shown the experimental data of freezing point measurements of mixtures of solutions of lead nitrate and potassium acetate in 1.2 M-KNO<sub>3</sub>.

The break in the curve (Fig. 1) indicates the proportion in which the complex formation takes place.

FIG. 1

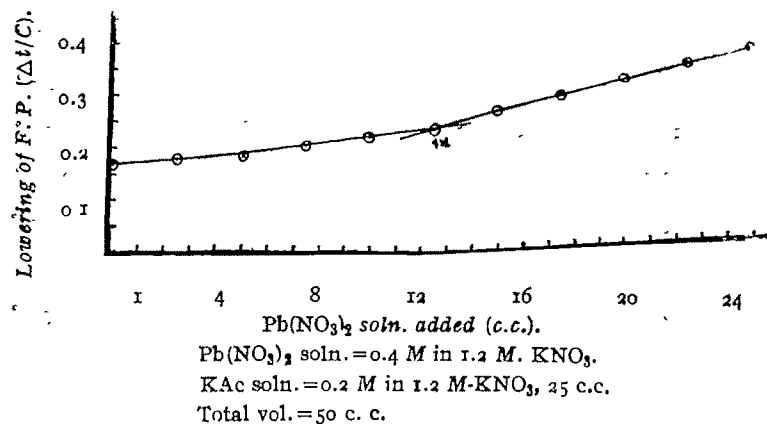


FIG. 2

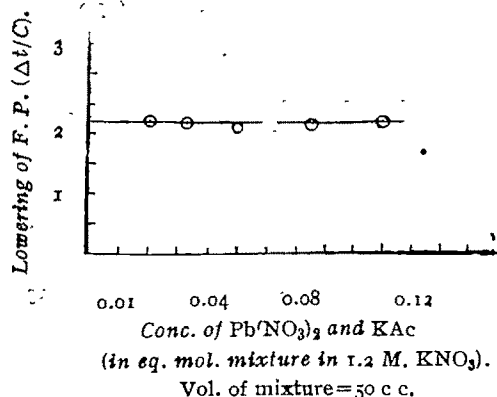
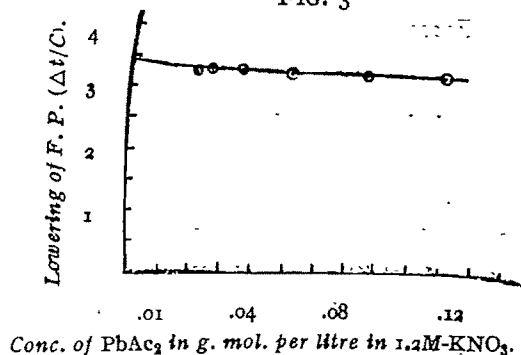


FIG. 3



Results of freezing point measurements of solutions containing mixtures of potassium acetate and lead nitrate in equimolecular proportions in 1.2 molar KNO<sub>3</sub> have been shown in Table II. Curve in Fig. 2 has been drawn to indicate the constancy of the value of  $\Delta t/C$  at different concentrations.

Table III and the accompanying curve in Fig. 3 show the data for freezing point measurements of pure lead acetate solutions in different concentrations in 1.2 M-KNO<sub>3</sub> solutions.

TABLE I

*Freezing point measurements of mixtures of 0.2 M-KAc in 1.2 M-KNO<sub>3</sub> and 0.4 M-Pb(NO<sub>3</sub>)<sub>2</sub> in 1.2 M-KNO<sub>3</sub> made up to 50 c.c. with 1.2 M-KNO<sub>3</sub>.*

0.2 M-KAc in 1.2 M-KNO <sub>3</sub> employed.	0.4 M-Pb(NO <sub>3</sub> ) <sub>2</sub> in 1.2 M-KNO <sub>3</sub> employed.	1.2 M-KNO <sub>3</sub> added.	F.P. of the mixture. (Beckmann).	Lowering of F.P. of the eutectic KNO <sub>3</sub> -H <sub>2</sub> O ( $\Delta t$ ).
0 c.c.	0 c.c.	50 c.c.	1.500°	
25	0	25	1.670°	0.170°
25	2.5	22.5	1.680°	0.180°
25	5	20	1.685°	0.185°
25	7.5	17.5	1.700°	0.200°
25	10	15	1.710°	0.210°
25	12.5	12.5	1.725°	0.225°
25	15	10	1.750°	0.250°
25	17.5	7.5	1.775°	0.275°
25	20	5	1.805°	0.305°
25	22.5	2.5	1.835°	0.335°
25	25	0	1.865°	0.365°

TABLE II

*Freezing point measurements of mixtures of equimolecular solutions of Pb(NO<sub>3</sub>)<sub>2</sub> and KAc in 1.2 M-KNO<sub>3</sub> in constant vol. of 50 c.c.*

Solutions employed.	F. P. registered (Beckmann).	Lowering of F. P. (Beckmann).	$\Delta t/C$ .
50 c.c. of 1.2 M-KNO <sub>3</sub>	1.500°		
25 c.c. of 0.2 M-KAc in 1.2 M-KNO <sub>3</sub> + 25 c.c. of 0.2 M-Pb(NO <sub>3</sub> ) <sub>2</sub> in 1.2 M-KNO <sub>3</sub> .	1.725°	0.225°	2.25
25 c.c. of 0.1 M-KAc in 1.2 M-KNO <sub>3</sub> + 25 c.c. of 0.1 M-Pb(NO <sub>3</sub> ) <sub>2</sub> in 1.2 M-KNO <sub>3</sub> .	1.605°	0.105°	2.15
25 c.c. of 0.6666 M-KAc in 1.2 M-KNO <sub>3</sub> + 25 c.c. of 0.6666 M-Pb(NO <sub>3</sub> ) <sub>2</sub> in 1.2 M-KNO <sub>3</sub> .	1.575°	0.075°	2.25
25 c.c. of 0.04 M-KAc in 1.2 M-KNO <sub>3</sub> + 25 c.c. of 0.04 M-Pb(NO <sub>3</sub> ) <sub>2</sub> in 1.2 M-KNO <sub>3</sub> .	1.545°	0.045°	2.25
25 c.c. of 0.15 M-KAc in 1.2 M-KNO <sub>3</sub> + 25 c.c. of 0.15 M-Pb(NO <sub>3</sub> ) <sub>2</sub> in 1.2 M-KNO <sub>3</sub> .	1.665°	0.165°	2.20

TABLE III

Freezing point measurements of lead acetate in diff. conc. in 1.2M-KNO<sub>3</sub>.

Solutions employed.	F. P. (Beckmann).	Lowering of F. P.	$\Delta t/C$ .
50 c.c. of 1.2 M-KNO <sub>3</sub>	1.500°		
50 c.c. of 0.1 M-Pb(Ac) <sub>2</sub> in 1.2 M-KNO <sub>3</sub>	1.840°	0.340°	3.4
50 c.c. of 0.075 M-Pb(Ac) <sub>2</sub> in 1.2 M-KNO <sub>3</sub>	1.455°	0.255°	3.4
50 c.c. of 0.05 M-Pb(Ac) <sub>2</sub> in 1.2 M-KNO <sub>3</sub>	1.670°	0.170°	3.4
50 c.c. of 0.03333 M-Pb(Ac) <sub>2</sub> in 1.2 M-KNO <sub>3</sub>	1.615°	0.115°	3.45
50 c.c. of 0.025 M-Pb(Ac) <sub>2</sub> in 1.2 M-KNO <sub>3</sub>	1.585°	0.085°	3.4
50 c.c. of 0.02 M-Pb(Ac) <sub>2</sub> in 1.2 M-KNO <sub>3</sub>	1.565°	0.065°	3.25

Assuming that the complex ion formed is  $Pb_2Ac_2^{++}$  from the reaction  
 $2Pb^{++} + 2Ac^{+} = Pb_2Ac_2^{++}$

we can get the value of the dissociation constant of this ion from the general equation of Job modified into the following form:

$$K = \frac{2C^3p[x(p+1)-1]^4}{(p-1)^3(1-2x)} \quad \dots (1)$$

where  $C$  = molar conc. of  $Pb^{++}$  ion in solution,  $p$  = molar conc. of  $Ac^{-}$  ion in soln and  $x$  c.c. of  $Ac^{-}$  combining with  $1-x$  of  $Pb^{++}$  produces the maximum changing effect.

Employing the data for the maximum change of conductivity given by Purkayastha and Sen Sarma (in Table VIII, *loc. cit.*) it has been found that a constant value for  $K$  in the above expression (1) can be had at different concentrations of the components, the average value being equal to  $43.67 \times 10^{-6}$ .

In the following table has been shown the theoretical value of the molecular lowering of freezing point of the system eutectic KNO<sub>3</sub>-H<sub>2</sub>O by the lead-acetato complex ion  $[PbAc]^{+}$  from the values of the degree of dissociation of the ion, calculated from the values of the dissociation constant  $K$  of the complex ion given by foregoing workers. The value of the molecular lowering of the freezing point, assuming the formation of the two-fold complex ion  $Pb_2Ac_2^{++}$ , has also been calculated and incorporated in the table.

TABLE IV

Authors.	$K$ .	$\alpha$ .	Mol. lowering of F.P.
Edmonds and Birnbow			
$PbAc^{+} = Pb^{++} + Ac^{-}$	$9.65 \times 10^{-3}$ at 25°	0.3636	2.328°
Purkayastha and Sen Sarma			
$PbAc^{+} = Pb^{++} + Ac^{-}$	$40.76 \times 10^{-3}$ at 30°	0.4662	2.492°
$Pb_2Ac_2^{++} = 2Pb^{++} + 2Ac^{-}$	$43.76 \times 10^{-6}$ at 30°	0.3450	3.5°

## DISCUSSION

It will appear from the data in Tables I and II and Figs. 1 and 2 that the values of the lowering of the freezing point of the system eutectic  $\text{KNO}_3\text{-H}_2\text{O}$  by solution molar with respect to both  $\text{Pb}^{++}$  and acetate ions is  $2.25^\circ$ . Assuming that such a solution contains the two-fold ion  $[\text{Pb}_2\text{Ac}_2]^{++}$  and its products of dissociation  $\text{Pb}^{++}$  and  $\text{Ac}^-$  ions, the total depression of freezing point of the system eutectic  $\text{KNN}_3\text{-H}_2\text{O}$  from the value of the degree of dissociation calculated in Table IV of the complex ion  $[\text{Pb}_2\text{Ac}_2]^{++}$  is found out to be equal to  $1.75^\circ$ . This value is much smaller than the experimental value  $2.25^\circ$ . The two-fold polymerised ion  $[\text{Pb}_2\text{Ac}_2]^{++}$  does not therefore exist.

The experimental value of the molecular depression of freezing point, however, agrees nearly with the value of depression calculated from Edmond and Birnbow's data and somewhat lower than that of Purkayastha and Sen Sarma (cf. Table IV).

However, the formation of the ion  $[\text{PbAc}]^+$  is certain as would appear both from the above calculations and the actual method of study employed by the present author.

The author expresses his grateful thanks to Prof. P. B. Sarkar, the University of Calcutta for kindly giving facilities in carrying out the present work in his laboratory.

LABORATORY OF THE GHOSH PROF. OF CHEMISTRY,  
UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,  
CALCUTTA.

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## STUDIES ON RANCIDITY OF BUTTERFAT. PART IV. PRELIMINARY INVESTIGATIONS ON FACTORS INFLUENCING RANCIDITY

By S. MUKHERJEE

A detailed study of the different factors influencing rancidity of butterfat has been carried out. The primary agent responsible for the development of rancidity is oxygen; the effect of light, moisture and micro-organisms are merely catalytic.

The enormous losses incurred in fats and oils, oil bearing foods and similar commodities due to the development of bad odour and taste, known generally as rancidity, have engaged the attention of numerous investigators. A vast literature has accumulated on this subject but as yet no clear understanding of the complete process is available. Various theories have been advanced and much experimental evidence has been adduced to substantiate one hypothesis or another and these have often resulted in confusing rather than clarifying the problem, and considerable doubt still exists as regards the actual agent or agents responsible for causing rancidity in fats and the mechanism of the process. Oxygen, moisture, light, certain metals and micro-organisms are the various agents proposed as the causes of rancidity in fats but it has not been answered with certainty whether it is a single agent that can produce the effect or a combination of two or more of these will be absolutely necessary to develop rancidity. Some of the workers claim that moisture and air together must act simultaneously, either of these alone being unable to produce rancidity and that light and micro-organisms are of secondary importance (Godbole and Sadgopal, *Z. Lebensm.*, 1936, 72, 36); some assert that light alone in the absence of air or oxygen is capable of producing rancidity, and air and moisture are not necessary (Wagner, Walker and Oestermann, *Z. unters Nahr-u- Genussm.*, 1913, 26, 704), while others claim that light and air are both essential to produce rancidity and that reports that exposure of fats to light alone is capable of producing rancidity *in vacuo* are erroneous (Schmalfuss, Werner and Gührke, *Marg. Ind.*, 1935, 26, 215, 242; Täufel, Thaler and Martinez, *ibid.*, 1933, 26, 37). As regards the action of micro-organisms, there is one school who hold that these agents play no part in producing rancidity (Duclaux, *Ann. Inst. Pasteur*, 1887; *Compt. rend.*, 1886, 102, 1077), while others believe that they act as simple catalysts and are not primarily responsible for the development of rancidity (Godbole *et al*, *loc. cit.*). It thus appears necessary to study whether one and only one factor is primarily responsible for the process, or association of one or more of these factors will be an absolute necessity for the onset of rancidity in fats.

In the ordinary process of development of rancidity in fats and oils it is sometimes very difficult to evaluate the effect of a specific environmental factor in the overall process, because in most cases several of these are simultaneously active. Of the several factors that may be operating, viz., oxygen, light, moisture, heat, micro-

organisms, etc. one may predominate under one set of conditions and quite a different one under another.

It therefore appears logical to carry out an investigation in which the effect of various environmental factors should be studied by making a careful control of the variables 'within relatively narrow limits'. In the experiments described in this paper, the effect of elimination of air, light, moisture and micro-organisms has been studied on the development of rancidity of butterfat on storage in glass vessels at 37° for a period of three months and the course of rancidity followed by determination of peroxide, Kreis and acid values. The following studies were undertaken:

- I. The effect of storage of butterfat in presence of air, light and moisture.
- II. The effect of storage of butterfat in presence of air and light (moisture only is absent).
- III. The effect of storage of butterfat in presence of air and moisture (light only is absent).
- IV. The effect of storage of butterfat in presence of light and moisture (air only is absent).
- V. The effect of storage of butterfat in presence of moisture only (both air and light are absent).
- VI. The effect of storage of butterfat in presence of light only (both air and moisture are absent).
- VII. The effect of storage of butterfat in presence of air only (both light and moisture are absent).
- VIII. The effect of storage of butterfat in presence of air, light and moisture, without previous sterilisation and exposed to atmospheric conditions.

#### EXPERIMENTAL

In all these experiments (Groups I-VII), the effect of micro-organisms was minimised by a preliminary sterilisation of the fat and using aseptic conditions as far as practicable during handling. The temperature effect was eliminated by storage in an incubator at 37°. The moisture content was determined by the A. O. A. C. method (cf. Methods of Analysis, A.O.A.C., 6th Ed., 1945, p. 501) using distillation with toluene and was found to be 0.20% and is always the same unless otherwise mentioned. Group VIII records experiments with fat stored as such without sterilisation in presence of air, light and moisture.

*Exclusion of Light.*—In experiments with Group III, V and VII light was excluded by storing the butterfat in 150 c.c. conical flasks (plugged with sterilised cotton wool), covered completely with black paper and placing the whole in the incubator.

*Exclusion of Moisture.*—In experiments with Groups II, VI and VII moisture was excluded as follows: The fat was first of all kept for 12 hours in a liquid state in an incubator at 39-40° in contact with one-tenth its weight of anhydrous  $\text{Na}_2\text{SO}_4$  (A.R.). The fat was then transferred to large (6" diam.) pyrex dishes which were thoroughly cleaned and dried in an air-oven at 200° for 2 days and then over a  $\text{P}_2\text{O}_5$  desiccator in vacuum (0.1 mm.) for a period of one month. The fat was then poured in

thin layers in such dishes and kept over  $P_2O_5$  in vacuum (0.1 mm) for one week in the dark before the actual experiment started. During handling the fat the effect of contamination from micro-organisms was reduced by working up inside a chamber sterilised with ultraviolet light for a period of 30 minutes. The fat thus dried was believed to be in all probability perfectly free from moisture and the result was checked by determination of moisture by the A.O.A.C. method which showed no measurable amount of moisture in the fat. But having regard to Baker's work on the influence of moisture in chemical reactions and the difficulty in removing the same absolutely from glass surface, it would be very difficult to assert whether insignificant traces of moisture were not present in the samples prepared; but for all practical purposes the samples might be treated as anhydrous.

*Exclusion of Air.*—In experiments with Groups IV and V, Thunberg's tubes were used for storage of fats with considerable advantage. The tubes were half-filled with the fat and the standard taper ground joint stopper put in place with a thin layer of vacuum grease and the tubes evacuated by means of a Cenco high vacuum pump for 4 hours, the stop-cock was closed, and the tube filled with pure nitrogen from a cylinder (freed from any oxygen by passage through alkaline pyrogallol and dried over  $CaCl_2$ ) drawn through a filter of sterilised cotton wool, and evacuated again for 2 hours, refilled with pure and dry nitrogen and again evacuated for 2 hours and finally kept filled with pure and dry nitrogen in order to prevent chances of leakage. A preliminary passage of pure nitrogen gas through the fat for several minutes before evacuation in Thunberg's tube was found advantageous for completely removing the last traces of oxygen. Here also aseptic conditions were rigorously followed as far as practicable in order to prevent contamination from micro-organisms such as operations inside a sterilised chamber and use of sterilised cotton filters during the passage of gas and during sampling of fat for determination of the values, use of sterilised pipettes and working inside sterilised chamber were strictly adhered to.

The peroxide value was determined by a modified Wheeler method, already indicated in Part II, as outlined below.

About 0.1 g. of the fat is weighted into a 500 c.c. glass-stoppered iodine bottle from which air has previously been excluded by flushing with  $CO_2$  for 3 to 5 minutes and 10 c.c. of a solvent comprising 40 parts  $CHCl_3$  and 60 parts A.R. acetic acid (glacial) are added to dissolve the fat. The solvent must be flushed with  $CO_2$  for 5-10 minutes before use to exclude any dissolved air. Saturated KI solution (2 c.c.) is next added and the stopper moistened with KI solution is put in place and the whole after thorough shaking kept in the dark for 1 hour after which the liberated iodine is titrated with 0.002N thiosulphate after diluting the reaction mixture with oxygen-free distilled water using 1% starch solution as the indicator. The peroxide value is expressed as the ml. of 0.002N thiosulphate required per g. of fat.

The acid value was determined by the usual method and expressed as percentage of free oleic acid (acid value  $\times 0.5031$ ). The Kreis test was performed by the method of Pool and Prater (*Oil & Soap*, 1945, **22**, 215). Since the procedure adopted differed in some minor detail from the original, the exact procedure is described below.

The fat (2 c.c.) is pipetted in a test tube (25 c.c.) and diluted to 5 c.c. with chloroform and treated with 5 c.c. of a 30% trichloroacetic acid in acetic acid solution and 1 c.c. of an 1% solution of phloroglucinol in glacial acetic acid. The resulting mixture is thoroughly shaken and the test tube is placed in a thermostat at  $40^{\circ} \pm 0.1^{\circ}$  and allowed to stand for exactly 15 minutes. After this time, the mixture is diluted with 5 c.c. (or 10 c.c.) of absolute alcohol and the colour matched in a Lovibond tintometer. The Kreis value has been expressed here as the number of Lovibond units per g. of fat. The analytical results are recorded in Table I (Groups I—VIII).

TABLE I

Peroxide, Kreis and acid values after

	15 days			30 days			45 days			60 days			85 days		
	*P.V.	K.	A.V.	P.V.	K.	A.V.	P.V.	K.	A.V.	P.V.	K.	A.V.	P.V.	K.	A.V.
Group I. Effect of storage of butterfat in presence of air, light and moisture at 37°.															
Sample I	0.15	0.1	0.2	0.30	1.6	0.45	2.5	4.3	0.71	3.2	8.8	1.3	19.0	12.6	2.1
Sample II	0.14	0.1	0.2	0.30	1.6	0.43	2.4	4.2	0.70	3.2	8.4	1.3	18.8	12.4	2.0
Sample III	0.13	0.1	0.2	0.28	1.6	0.41	2.3	4.1	0.70	3.0	8.0	1.3	18.8	12.4	2.0
Mean	0.14	0.1	0.2	0.29	1.6	0.43	2.4	4.2	0.70	3.1	8.3	1.3	18.9	12.5	2.0
Group II. Effect of storage of butterfat in presence of air and light at 37°.															
Sample I	0.10	0.0	0.0	0.18	1.3	0.0	1.0	2.4	0.10	1.8	3.8	0.30	8.5	6.0	0.37
Sample II	0.10	0.1	0.0	0.20	1.3	0.0	1.2	2.5	0.10	2.0	3.8	0.30	8.5	6.0	0.41
Sample III	0.10	0.0	0.0	0.21	1.4	0.0	1.0	2.5	0.15	2.0	4.0	0.31	8.5	6.0	0.43
Mean	0.10	—	0.0	0.20	1.3	0.0	1.1	2.5	0.12	1.9	3.9	0.30	8.5	6.0	0.40
Group III. Effect of storage of butterfat in presence of air and moisture at 37°.															
Sample I	0.08	0.0	0.18	0.15	1.0	0.30	0.50	3.0	0.60	2.0	6.0	0.95	10.8	8.0	1.8
Sample II	0.10	0.0	0.18	0.15	1.0	0.30	0.51	3.1	0.60	2.0	6.5	0.96	10.9	8.1	1.9
Sample III	0.09	0.0	0.17	0.14	1.0	0.28	0.50	3.0	0.50	2.0	5.6	0.94	10.8	8.0	1.7
Mean	0.09	0.0	0.18	0.15	1.0	0.29	0.50	3.0	0.57	2.0	6.0	0.95	10.8	8.0	1.8
Group IV. Effect of storage of butterfat in presence of light and moisture at 37°.															
Sample I	0.0	0.0	0.0	0.0	0.0	0.11	0.0	0.0	0.20	0.0	0.0	0.71	0.10	0.1	0.95
Sample II	0.0	0.0	0.0	0.0	0.0	0.08	0.0	0.0	0.19	0.0	0.0	0.50	0.00	0.0	0.90
Sample III	0.0	0.0	0.0	0.0	0.0	0.11	0.0	0.0	0.20	0.0	0.3	0.66	0.02	0.0	0.91
Mean	0.0	0.0	0.0	0.0	0.0	0.10	0.0	0.0	0.20	0.0	0.0	0.62	0.04	—	0.92
Group V. Effect of storage of butterfat in presence of moisture alone at 37°.															
Sample I	0.0	0.0	0.0	0.0	0.0	0.02	0.0	0.0	0.19	0.0	0.0	0.90	0.00	0.0	1.10
Sample II	0.0	0.0	0.0	0.0	0.0	0.05	0.0	0.0	0.20	0.0	0.0	0.92	0.05	0.3	1.10
Sample III	0.0	0.0	0.0	0.0	0.0	0.06	0.0	0.0	0.25	0.0	0.0	0.96	0.10	0.6	1.25
Mean	0.0	0.0	0.0	0.0	0.0	0.04	0.0	0.0	0.21	0.0	0.0	0.93	0.05	0.3	1.15
Group VI. Effect of storage of butterfat in presence of light only at 37°.															
Sample I	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.16	0.0	0.0	0.20	0.02	0.1	0.40
Sample II	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.18	0.0	0.0	0.20	0.02	0.1	0.41
Sample III	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.15	0.0	0.0	0.18	0.02	0.0	0.40
Mean	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.16	0.0	0.0	0.19	0.02	0.1	0.40



TABLE I (contd.)

	15 days			30 days			45 days			60 days			85 days		
	P.V.	K.	A.V.	P.V.	K.	A.V.	P.V.	K.	A.V.	P.V.	K.	A.V.	P.V.	K.	A.V.
Group VII. Effect of storage of butterfat in presence of air only at 37°.															
Sample I	0.08	0.0	0.0	0.15	0.1	0.0	1.1	0.8	0.05	2.0	2.4	0.20	7.5	3.3	0.41
Sample II	0.08	0.0	0.0	0.14	0.1	0.0	1.0	0.8	0.04	2.0	2.3	0.15	7.5	3.2	0.40
Sample III	0.08	0.1	0.0	0.12	0.1	0.0	1.0	0.7	0.02	2.0	2.3	0.10	7.2	3.1	0.40
Mean	0.08	—	0.0	0.14	0.1	0.0	1.0	0.8	0.05	2.0	2.3	0.15	7.4	3.2	0.40
Group VIII. Effect of storage of butterfat (in presence of air, light, moisture) without sterilisation and exposed to atmospheric condition.															
Sample I	0.15	0.1	0.2	0.20	1.0	0.50	2.0	3.0	1.2	2.8	4.6	1.50	12.0	6.9	4.2
Sample II	0.15	0.1	0.2	0.20	0.8	0.50	1.9	2.7	1.0	2.3	4.4	1.45	10.6	7.0	2.6
Sample III	0.15	0.1	0.2	0.20	0.3	0.51	2.0	2.8	1.1	2.5	4.6	1.47	11.2	7.3	4.0
Mean	0.15	0.1	0.2	0.20	0.7	0.50	2.0	2.8	1.1	2.5	4.5	1.47	11.3	7.0	3.9

\* P.V. stands for peroxide value, A.V. for acid value and K for Kreis No.

Rancidity as detected by taste and smell developed quickly in experiments of Groups I and VIII within 45 days and more slowly with those in Groups II, III and VII (after 60 days), but with samples of Groups IV, V and VI there was no detectable off-flavour which was so characteristic in the control samples (Group I). These results were well corroborated by peroxide and reis Ktests. From the above table the following conclusions were drawn :

In the absence of any influence of micro-organisms, hydrolytic rancidity as measured by development of free acidity proceeds only in presence of moisture, though slight acidity develops even under conditions where moisture is not present (cf. Table I, Groups II, VI and VII), but oxidative rancidity as determined by peroxide and Kreis values is observed only where air (*i.e.* oxygen) is present (cf. Table I, Groups I, II, III and VII), exclusion of air practically stops such rancidity (cf. Table I, Groups IV, V and VI). The part played by light is only one of positive catalyst (Table I, Groups I and III) in that it causes an acceleration of the rate of the reaction, the development of peroxides is diminished to a considerable extent when this factor is absent (cf. Table I, Groups I, II and III). The development of peroxide is again greater whenever the acidity is greater ; this tends to show that moisture in bringing about accelerated hydrolysis of fats provides more easily oxidisable free fatty acids (at least more active than the glycerides themselves) resulting in an increased peroxide value (cf. Table I, Groups I, II, III and IV). In Group VII oxygen in absence of moisture and light fails to bring about as much rancidity as it can when moisture is present (Group III). The Kreis figures are generally in keeping with peroxide figures.

When the samples are exposed to atmospheric conditions and subject to contamination from micro-organisms (Group VIII), the peculiarity is that an acceleration in the rate of hydrolysis is noticed in the samples accompanied by a much less amount of peroxide. All these samples responded to Taufel-Thaler reaction for ketones (negative with Groups I-VII) at the end of the experiments. The behaviour of micro-organisms

has been separately studied elsewhere, but from the experiments described here it may be said that rancidity in butterfat can be developed without these agencies, and such organisms cannot be the primary causes of rancidity.

One thing of particular interest is that once a certain peroxide level is reached (approximately 2.0), the rate of oxidation is increased remarkably; this therefore definitely indicates the termination of the induction period of the fat.

#### CONCLUSIONS

The fundamental and primary cause of rancidity in fats is the action of oxygen or air.

The function of light and moisture in the development of rancidity is merely catalytic, and rancidity can as well develop in the absence of such environmental factors. The action of moisture is primarily to cause hydrolysis of the glycerides. But rancidity may develop in fats by oxidation of the latter without undergoing a previous hydrolysis. As regards the relative efficiency of light and moisture in developing rancidity and off-flavour, it is very difficult to differentiate between them and state which is more prominent than the other. Fats keep better in the absence of moisture or light than in presence of it.

Micro-organisms are not primarily responsible for the onset of rancidity in fats but they play an important part in such degradation reactions and give positive evidence of a new type of rancidity characterised by increased hydrolysis and ketone formation.

In subsequent papers, the effect of the various factors such as temperature, oxygen concentration, light intensity, metallic catalysts and other chemical accelerators on the autoxidation has been studied in much greater detail.

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DEPARTMENT OF APPLIED CHEMISTRY,  
UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA.

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# DIELECTRIC CONSTANT AND DIPOLE MOMENT OF HYDROGEN HALIDES

By S. K. K. JATKAR AND (MISS) S. B. KULKARNI

The dipole moments of hydrogen halides in solid and liquid state and in solutions in various polar and non-polar solvents have been calculated by applying the new equation. Unlike the Debye's values the new moments are in agreement with the gas values. The moments are independent of solvent and temperature. The ionic character of hydrogen halides is an inverse function of the square of the internuclear distance.

The success of Debye-Clausius-Mosotti (D.C.M.) equation (*Physikal. Z.*, 1912, 13, 97) showing the relationship between the dielectric constant and dipole moment in the case of gases and dilute solutions in non-polar solvents is not reflected in its application to the case of concentrated solutions in both non-polar and polar solvents and to normal and associated liquids. In dilute solutions the solvation has vitiated the results. No equation has so far been proposed to explain the high dielectric constant of associated liquids, rotating solids and solutions in polar solvents.

The equations put forth are summarised below :

(1) D.C.M. (*loc. cit.*).

$$(\epsilon - 1) \frac{M}{d} = \frac{4\pi N}{3} \times (\epsilon + 2) \left( \alpha + \frac{\mu^2}{3kT} \right) \text{ for liquids and solutions.}$$

$$(\epsilon - 1) \frac{M}{d} = 4\pi N \left( \alpha + \frac{\mu^2}{3kT} \right) \text{ for gases } \epsilon \approx 1$$

$$\text{therefore } (\epsilon - n^2) \frac{M}{d} = \frac{4\pi N \mu^2}{3kT} \text{ for gases.}$$

(2) Pauli (*Z. Physik*, 1921, 6, 219).

$$(\epsilon - n^2) \frac{M}{d} = N \left( \frac{C \mu^2}{kT} + \alpha \right)$$

(3) Onsager (*J. Amer. Chem. Soc.*, 1936, 58, 1486).

$$(\epsilon - n^2) \frac{M}{d} = \frac{4\pi N \mu^2}{9kT} \times \frac{\epsilon(n^2 + 2)^2}{2\epsilon + n^2}$$

(4) Kirkwood (*J. Chem. Phys.*, 1939, 7, 94).

$$(\epsilon - n^2) \frac{M}{d} = \frac{9}{2} \times \frac{(n^2 + 2)^2}{3} \times \frac{1}{1 + \frac{n^2}{2\epsilon}} \times gB$$

$$\left( B = \frac{4\pi N \mu^2}{9kT}; g = \text{constant} \right)$$

(5) Frölich and Sack (*Proc. Roy. Soc.*, 1944, **A**, 182, 388).

$$\begin{aligned} (\epsilon - n^2) \frac{M}{d} &= \frac{4\pi N \mu^2}{a^3 kT} \times \frac{3\epsilon}{2\epsilon + n^2} \times (1 + \gamma/2) \\ &= \frac{4\pi N \mu^2}{3kT} \times \frac{3\epsilon}{2\epsilon + n^2} \left[ 1 + \frac{1}{3} \frac{(\epsilon - n^2)^2}{n^2} \right] \end{aligned}$$

(6) Jatkar (*Nature*, 1944, **153**, 224).

$$(\epsilon - n^2) \frac{M}{d} = \frac{4\pi N \mu^2}{3kT} \cdot \frac{j+1}{j} \quad (j = \frac{1}{2} \text{ for liquids \& solids and } j = \infty \text{ for gases}).$$

Bottcher (*Physica*, 1939, **6**, 59) has published numerous papers showing the applicability of Onsager's equation to the dielectric constant of pure liquids. Wilson (*Chem. Rev.*, 1939, **25**, 377) has adversely criticised Onsager's equation as theoretically surprising and probably fortuitous in agreement.

Frölich and Sack (*loc. cit.*) have stated that for liquids with low viscosity there are no deviations from Onsager's theory which unfortunately is not the case because the dielectric constants of ethyl ether, chloroform, acetone and so on do not follow Onsager's equation.

In a series of papers published by Jatkar (*loc. cit.*) and Jatkar *et al.* (*J. Indian Inst. Sci.*, 1946, **28A**, Part II; 1947, **30A**, Part IV; *Indian J. Phys.*, 1948, **22**, 431; 453; 1949, **23**, 145; *Curr. Sci.*, 1949, **18**, 76, 130) a remarkably simple relationship between the dielectric constant and dipole moment of liquids has been derived on the basis of assumptions inherent in previous theories.

The new equation is derived on the basis that a dipole is needle-shaped and that it has two possible settings in the electrical field, one parallel and another antiparallel to the direction of the field owing to the hindered rotation in liquids and solids. Since  $2j+1$  is the total number of positions,  $2j+1=2$  or  $j=1/2$  for liquids and solids.

It is obvious that no simple single relationship can be postulated to take into account the complex nature of liquids.

In the present paper we have shown the application of the new equation to the dielectric constants of hydrogen halides in solid, liquid and solutions by applying both the Debye and the Onsager equations.

The dipole moments of hydrogen halides have formed the subject of numerous researches. Dielectric polarisations of HCl, HBr and HI have been measured by Fairbrother in different polar and non-polar solvents and the moments are calculated by applying the D.C.M. equation. The measurements by Fairbrother (*J. Chem. Soc.*, 1933, 1541, *Trans Faraday Soc.*, 1934, **30**, 388) in non-polar solvents like benzene, carbon tetrachloride, etc., exhibit a positive solvent effect. In ethyl bromide and ethylene dichloride, however, practically normal values (1.02D and 0.97D) were obtained for the moment of HCl. Recently Weith *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 805) have confirmed the positive solvent effect for HCl and HBr. The higher moments obtained in solutions have been

attributed to the increase of the electron density at the halogen end of the molecule, and in dioxane solutions there is an incipient ionisation of these solutes.

Smyth and Hitchcock (*J. Amer. Chem. Soc.*, 1933, **55**, 1831) have studied the dielectric constant of pure hydrogen halides at low temperatures in solid state, and Glockler and Peak (*J. Chem. Phys.*, 1936, **4**, 659) have measured the values for pure liquid HCl. The dielectric constant-temperature curves show that there is a rotation in solid state, which is confirmed by the study of specific heats.

It is not possible to calculate the moment of pure solids and liquids with the help of Debye's equation. The application of Onsager's equation to the dielectric constant of pure hydrogen halides would be interesting in as much as these compounds correspond to the model of a sphere. While the Onsager's moment for liquid HCl is 1.07, the value for liquid HBr is 0.90, which is too high. A simple and straightforward explanation of all high dielectric constants of liquids and solids is given by the new relationship found by Jatkar (*loc. cit.*) between the dielectric constant of liquids and solids and the dipole moment of free molecules.

The authors have calculated the moments of halogen hydrides in solid and liquid state and also in solutions by applying the new and simple relationship,

$$P = (\epsilon - 1)M/d; P_s = (n^2 - 1)M/d; P - P_s = 4\pi N\mu^2/kT$$

for pure solids and liquids, and

$$P_{12} = (\epsilon_{12} - 1) \frac{M_1 f_1 + M_2 f_2}{d_{12}} = P_1 f_1 + P_2 f_2 \text{ and}$$

$$P_2 - P_s = 4\pi N\mu^2/kT \text{ for solutions.}$$

#### Hydrogen Fluoride

The high dielectric constant of liquid HF (174.3 at  $-73^\circ$  and 83.6 at  $0^\circ$ ) cannot be explained on the basis of the Hexamer structure of HF at low temperature unless one adopts the proton transition theory, the hydrogen oscillating between two fluorine atoms. On the other hand, if one postulates a high degree of flexibility of HF held by hydrogen bonds, the rotation will be of hindered type and there should exist a transition temperature for the liquid as in the case of other hydrogen bonded liquids like methyl alcohol, water, etc. Using a modified equation

$$(\epsilon - n^2) M/d = 4\pi N\mu^2/k(T - \theta)$$

a value of  $-120^\circ\text{C}$  for  $\theta$  would yield 1.88 as the dipole moment in liquid HF as compared to the value of 1.91 for the gas (cf. Smyth and Hanney, *J. Amer. Chem. Soc.*, 1946, **68**, 171). According to Weith's measurements the electric moments of HF are 1.9, 2.0, 2.2 and 2.34 in  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ ,  $n\text{-C}_7\text{H}_{16}$  and  $\text{C}_4\text{H}_8\text{O}_2$ . Unfortunately no data are available to enable a recalculation of these results.

*Electronic Polarisation.*—The new value of electronic polarisation  $P_s = (n^2 - 1)M/d$  is calculated from the refractive index and density data given by Smyth (*Proc. Roy. Soc.*, 1912, **A**, 87, 336) and assumed to be independent of temperature.

TABLE I

Substance.	Temp.	Density.	Ref. index.	$P_2$ .
HCl	10.5°	0.854	1.254	24.5
HBr	10.0°	1.630	1.325	37.5
HI	12.0°	2.270	1.466	64.8

The results are given in the following tables.

TABLE II

*Dielectric constant and dipole moments of hydrogen halides.*

(Pure liquids and solids).

Substance.	$t^\circ(\text{C})$ .	$\epsilon$ .	$P$ .	$\mu \times 10^{18}$ .
HCl	-173°	17.25	415.6	0.83
(solid)	-143	15.38	366.9	0.89
(a)	-117	14.53	345.3	0.94
HCl	-112	14.05	375.2	1.00
(liquid)	-66.5	8.92	253.0	0.91
(b)	-15.0	6.33	198.0	0.90
HBr	-165.5	11.86	358.74	0.78
(solid)	-140.5	8.45	246.09	0.70
(a)	-124.8	8.30	241.14	0.73
HBr	-87.5	8.48	247.08	0.83
(liquid)	-85.0	7.00	218.50	0.76
(a)	-70.0	6.40	202.10	0.77
HI	-143.0	4.50	144.8	0.43
(solid)	-117.0	4.20	133.3	0.44
(a)	-85.0	3.96	124.2	0.45
HI	-53.0	3.87	120.2	0.47
(liquid)	-50.0	3.38	106.6	0.42
(a)	-37.0	3.27	103.5	0.40

(a) Smyth and Hitchcock, *J. Amer. Chem. Soc.*, 1933, 55, 1831.

(b) Glockler and Peak, *J. Chem. Phys.*, 1936, 4, 659.

TABLE III

*Dipole moments of hydrogen halides in various solvents.*

Solvent.	$t^\circ$ .	$f_2$ .	$\epsilon$ .	$d$ .	$P_2$ .	$\mu \times 10^{18}$ .
			(1) HCl.			
$\text{C}_6\text{H}_6(c)$	25°	0.0069	2.288	0.8733	237.39	1.06
		0.0203	2.317	0.8742	236.26	1.06
		0.0302	2.339	0.8746	237.50	1.06
$\text{CCl}_4(c)$	25°	0.0026	2.232	1.5835	291.92	1.19
		0.0107	2.247	1.5811	244.02	1.07
$\text{C}_6\text{H}_{12}(c)$	25°	0.0039	2.018	0.7737	223.33	1.01
		0.0101	2.028	0.7740	215.65	1.00

TABLE III (contd.)

Solvent.	$t^\circ$	$f_2$	$\epsilon$	$d$	$P_2$	$\mu \times 10^{18}$
$C_2H_4Cl_2$ (d)	20°	0.0246 0.0194 0.0167	10.561 10.571 10.580	1.2521 1.2528 1.2533	237.51 252.58 240.31	1.05 1.08 (1.15)
(2) HBr						
$C_6H_6$ (e)	20°	0.0489 0.0407 0.0221	2.342 2.334 2.310	0.9040 0.8996 0.8899	158.65 157.15 164.45	0.79 0.78 0.81
$CCl_4$ (e)	20°	0.0346 0.0154 0.0102	2.266 2.250 2.246	1.5982 1.5958 1.5951	136.29 142.09 146.95	0.71 0.73 0.73
(3) HI						
$C_6H_6$ (e)	20°	0.0654 0.0370 0.0244	2.307 2.297 2.294	0.9435 0.9153 0.9028	94.86 95.25 99.92	0.40 0.41 0.43
$CCl_4$ (e)	20°	0.0459 0.04231 0.02692	2.246 2.245 2.242	1.6156 1.6142 1.6069	85.64 84.14 84.58	0.33 0.32 0.32

(c) Fairbrother, *J. Chem. Soc.*, 1932, 43.(d) Fairbrother, *ibid.*, 1933, 1541.(e) Fairbrother, *Trans. Faraday Soc.*, 1934, 30, 862.

TABLE IV

Solvent.	D.C.M.(1) (sol)	$\mu \times 10^{18}$		Gas D.C.M.(1)	Solvent.	D.C.M.(1) (sol)	$\mu \times 10^{18}$		Gas D.C.M.(1)
		New.	Onsager.				New.	Onsager.	
		(1) HCl					(2) HBr		
Pure solid	—	0.90	—	—	Pure solid	—	0.79	—	—
Liquid	—	0.99	1.07	1.03	Pure liquid	—	0.76	0.90	0.78
C <sub>6</sub> H <sub>6</sub>	1.26	1.06	—	1.06	C <sub>6</sub> H <sub>6</sub>	1.00	0.79	—	—
CCl <sub>4</sub>	1.32	1.07	—	—	CCl <sub>4</sub>	0.96	0.72	—	—
C <sub>6</sub> H <sub>12</sub>	1.32	1.01	—	—	(3) HI				
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	0.97	1.10	—	—	Pure solid	—	0.44	—	—
					Pure liquid	—	0.40	—	0.38
					C <sub>6</sub> H <sub>6</sub>	0.58	0.41	—	—
					CCl <sub>4</sub>	0.50	0.33	—	—

D.C.M. equation (1).

## DISCUSSION

The density of solid hydrogen halides is not known at low temperatures, specially near the transition temperature where large changes in density take place. The authors have taken the density at melting point for the purpose of calculation. Hence the results, specially for solids near the transition point, are not as satisfactory as could

be expected. It is very remarkable that the moments calculated in solid and liquid state and solutions by applying the new equation are nearly the same as those for gases, except the moment of HCl calculated from the data in ethyl bromide (1.4 D). The moments are independent of temperatures and solvents.

The higher values in solution reported in literature are thus due to the application of D.C.M. equation and the explanations of higher moments in solution advanced by Fairbrother are unnecessary. In the case of solutions in non-polar solvents ( $\epsilon \approx 2.5$ ) it can be shown (Jatkar *et al.*, *loc. cit.*, 1947) that  $\mu_{\text{D.C.M.}} / \mu_{\text{new}} > 1.4$  when  $P_{\text{D.C.M.}} > P_2$  (D.C.M.). The so-called solvent effect in the case of hydrogen halides is due to this factor. If the solvent is polar (*i.e.*  $\epsilon > 2.5$ ) then the ratio  $\mu_{\text{D.C.M.}} / \mu_{\text{new}}$  is less than 1.4.

The ionic natures as calculated from the dipole moment data  $i = \mu / e.d.$  are 0.43, 0.17, 0.11 and 0.05 for HF, HCl, HBr and HI. The present authors (Jatkar *et al.*, *loc. cit.*, 1949) have pointed out a simple relationship between the ionic nature and the internuclear charges,  $i = (Z_A / Z_A + Z_B) n$ , where  $Z_A$  and  $Z_B$  are the nuclear charges of the atoms A and B and  $n$  is a constant which is  $8/3$  in the case of hydrogen halides.

TABLE V

Bond.	Distance.	$Z_A / Z_A + Z_B$ .	$n$ .	Ionic Calc. ( $Z_A / Z_A + Z_B$ ) $n$ .	nature Obs. $\mu / e.d.$
HF	0.92	0.100	8/3	0.27	0.43
HCl	1.28	0.056	8/3	0.15	0.17
HBr	1.43	0.028	8/3	0.074	0.11
HI	1.63	0.018	8/3	0.049	0.052

The calculated ionic nature of HF, while in agreement with the bond energy data (Jatkar and Kulkarni, *Curr. Sci.*, 1949, **18**, 131) is lower than the observed value 0.43. It is interesting to point out the inverse relationship between the ionic nature and the square of the internuclear distance in the case of HF, HCl, HBr and HI.

DEPARTMENT OF PURE AND APPLIED CHEMISTRY,  
INDIAN INSTITUTE OF SCIENCE, BANGALORE 3.

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## ANALYTICAL CHEMISTRY OF THORIUM. PART III. SEPARATION FROM CERITE EARTHS WITH *o*-TOLUIC ACID AND ACETYL-SALICYLIC ACID

BY B. R. LAKSHMANA RAO AND BH. S. V. RAGHAVA RAO

From solutions just neutral to Congo red, *o*-toluic acid precipitates thorium quantitatively and also affords a method of separating the cerite earths, if the amount of the latter is not higher than ten-fold. The  $p_H$  of the liquid, which is not critical, falls between 3 and 4. Acetylsalicylic acid exhibits a similar behaviour, but the presence of ammonium acetate is necessary. When the  $\text{ThO}_2 : \text{R}_2\text{O}_3$  ratio is not greater than 5, double precipitation is necessary. The  $p_H$  of the liquid in this case lies between 4 and 4.4. Both the reagents have been employed for the estimation of thorium in monazite

In this communication the use of *o*-toluic acid and acetylsalicylic acid as reagents for the separation of thorium from cerite earths in monazite is described. The former of the reagents gives satisfactory separation in a single operation when  $\text{ThO}_2 : \text{R}_2\text{O}_3$  is not over 10 ; thus it enables thorium in Indian monazite (when the ratio is 1.8) to be estimated in one operation. Acetylsalicylic acid does not precipitate thorium in the cold ; precipitation begins on heating the solution and is complete only on the addition of ammonium acetate. In a way, precipitation of thorium by this reagent may be considered a "homogeneous process". The advantages of precipitation in a homogeneous solution have been discussed by Willard, Gordon and Vanselow (*Anal. Chem.*, 1949, 21, 1323.)

### EXPERIMENTAL

**Reagents.**—The preparation of pure thorium nitrate as well as the cerite earth solution has been described in an earlier communication (Part I, this *Journal*, 1950, 27, 457). Both *o*-toluic acid and acetylsalicylic acid were obtained by recrystallising B. D. H. reagent grade chemicals several times until the melting points coincided with the theoretical values, 102° and 135° respectively.

#### *o*-Toluic Acid

**Estimation.**—The thorium solution is just neutralised to Congo red and diluted to 100 ml. The liquid is boiled and the thorium is precipitated by the addition of a boiling 0.5% solution of *o*-toluic acid. The white flocculent precipitate which results immediately settles quickly if the boiling is continued for two minutes. It is then set aside for 30 minutes, filtered through a 11 cm. Whatmann No. 41 filter paper, washed first with 0.05% *o*-toluic acid, finally with water and ignited wet. Table I shows the results obtained

TABLE I

*Estimation of thorium.*

Expt. No.	ThO <sub>2</sub> taken.	ThO <sub>2</sub> obtained.	Difference.
1	0.0748 g.	0.0749 g.	+0.1 mg.
2	0.1496	0.1496	0
3	0.2992	0.2993	+0.1
4	0.0374	0.0375	+0.1
5	0.0094	0.0093	-0.1

The smallest amount of ThO<sub>2</sub> that could be estimated by this procedure was 0.0094 g. A precipitate occurs even at lower concentration, i.e., 4 to 5 mg., but it is too small to handle with any ease.

*Separation.*—*o*-Toluic acid precipitates the cerite earths incompletely from solutions which are definitely alkaline. Advantage is therefore taken of this difference in behaviour, and the  $p_H$  of the solution is adjusted to the optimum value. Excellent separation is achieved in the  $p_H$  range 3-4 which is established finally when the thorium solution is made just neutral to Congo red. Thus, the procedure detailed for the estimation may be conveniently adopted for its separation from cerite earths. Table II gives the results of test separations.

TABLE II

Expt. No.	ThO <sub>2</sub> taken.	Cerite earths added.	ThO <sub>2</sub> found.	Difference.
1	0.1496 g.	0.09 g.	0.1497 g.	+0.1 m.g.
2	"	0.18	0.1495	-0.1
3	"	0.36	0.1495	-0.1
4	"	0.72	0.1497	+0.1
5	"	1.44	0.1496	0
6	"	1.62	0.1497	+0.1

The ThO<sub>2</sub> is pure white in all cases.

*Determination of Thorium in Monazite.*—The decomposition of monazite has been described in an earlier communication (*loc. cit.*). The thorium in the extract, which has been freed from zirconium and phosphoric acid, has been estimated by the *o*-toluic acid method and compared with the values obtained with *m*-nitrobenzoic acid after double precipitation.

TABLE III

Expt. No.	Volume of monazite extract taken.	Th O <sub>2</sub> estimated with <i>o</i> -toluic acid.	Th O <sub>2</sub> estimated with <i>m</i> -nitrobenzoic acid.
1	10 ml.	0.1101 g.	0.1102 g.
2	10	0.1102	0.1102
3	20	0.2205	0.2205
4	20	0.2206	0.2205

*Acetylsalicylic Acid*

When a cold saturated solution of acetylsalicylic acid is added to a cold solution of thorium nitrate or chloride in the  $p_H$  range of 2.6 to 3.8, no precipitation takes place even after long standing. When the liquid is heated to boiling, gradual separation of the thorium salt occurs, and the thorium recovery is 97 to 98%. If, however, 10 ml. of a 5% ammonium acetate solution are added, precipitation of thorium is complete.

*Procedure.*—The following procedure is recommended both for the estimation of thorium and the separation of cerite earths therefrom. The slightly acid solution of thorium or thorium and cerite earths is neutralised to Congo red with careful addition of dilute ammonia and diluted to 100 ml. 10 ml. of 5% ammonium acetate are then added and the liquid is heated to boiling. To the boiling solution are then added with continuous stirring 50 ml. of 1% boiling acetylsalicylic acid. The boiling is continued for a minute after, and the liquid is set aside in a warm place. The precipitate settles rapidly. It is then filtered through a 11 cm. Whatmann No. 41 filter, washed with 0.05% acetylsalicylic acid in 0.05% ammonium acetate, partially dried, and ignited to the oxide.

When the cerite earth—thorium ratio is over 5, small quantities of the former are carried down with the thorium precipitate. These are, however, removed completely in a second precipitation. The thorium precipitate is dissolved in 1:1 nitric acid, receiving the filtrate in the original beaker and the liquid is neutralised as before to Congo red. Precipitation with the reagent is repeated after the addition of ammonium acetate.

Under these conditions a  $p_H$  of 4.0 to 4.4 is established in the final liquid. Preliminary experiments have shown that below  $p_H$  3.8 the precipitation of thorium by this reagent is not complete, while at about 4.8, the cerite earths also separate from the solution. Tables IV and V give some of the results obtained.

TABLE IV

*Estimation of thorium with<sup>2</sup>acetylsalicylic acid.*

Expt. No.	ThO <sub>2</sub> present.	ThO <sub>2</sub> obtained.	Difference.
1	0.0573 g.	0.0572 g.	-0.1 mg.
2	0.1146	0.1146	0
3	0.2292	0.2293	+0.1

TABLE V

*Separation of cerite earths from thorium.*

Expt. No.	ThO <sub>2</sub> taken.	Cerite earths added.	ThO <sub>2</sub> obtained*.	Difference.
(a) Single precipitation.				
1	0.0573 g.	0.09 g.	0.0573 g.	0 mg.
2	0.0573	0.18	0.0572	-0.1
3	0.0573	0.27	0.0574	+0.1
4	0.0573	0.36	0.0581	+0.8

TABLE V (contd.)

Expt. No	ThO <sub>2</sub> taken.	Cerite earths added	ThO <sub>2</sub> obtained*.	Difference
(b) Double precipitation.				
5	0.0573 g.	0.36 g	0.0572 g.	-0.1 mg.
6	0.0573	0.45	0.0574	+0.1
7	0.0573	0.90	0.0573	0

\* Mean of two successive determinations.

*Estimation of Thorium in Monazite.*—Thorium in measured quantities of monazite extract (cf. *o*-toluic acid) was estimated by a double precipitation with the reagent. Table VI gives the results obtained.

TABLE VI

Expt. No.	Volume of monazite extract.	Th O <sub>2</sub> found with	
		<i>m</i> -nitrobenzoic acid.	acetylsalicylic acid.
1	10 ml.	0.1102 g.	0.1103 g.
2	10	0.1102	0.1104
3	20	0.2204	0.2204
4	20	0.2204	0.2203

CHEMICAL LABORATORIES,  
ANDHRA UNIVERSITY, WALTAIR.

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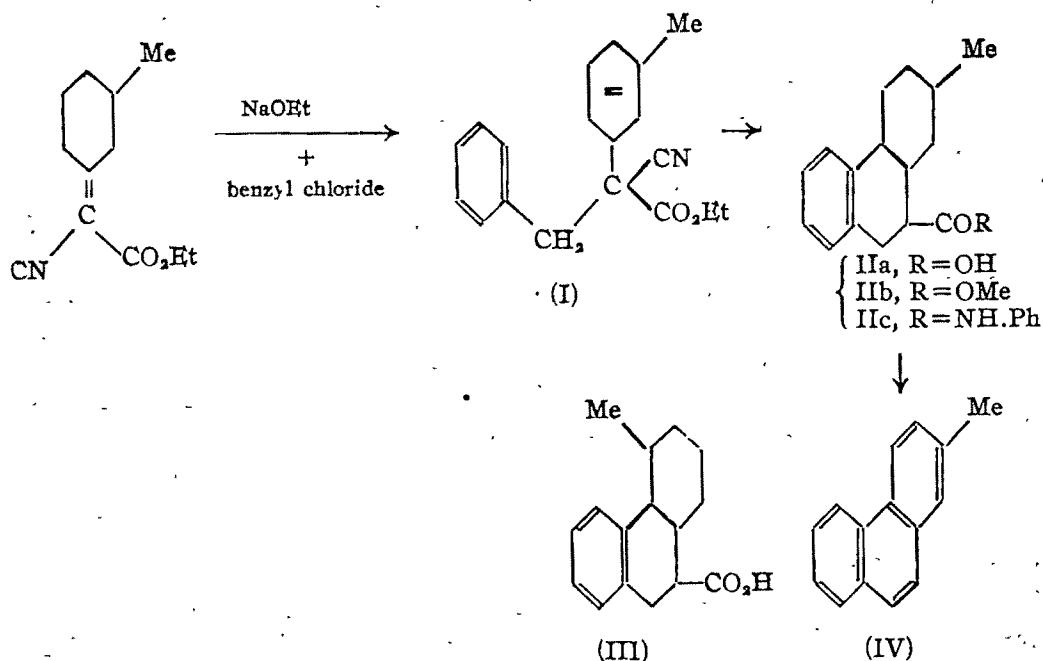
## A NEW SYNTHESIS OF 2-METHYLPHENANTHRENE

BY PASUPATI SEN GUPTA\* AND BIDYUT KAMAL BHATTACHARYYA

Ethyl 3-methylcyclohexylidene-cyanoacetate has been condensed with benzyl chloride in the presence of sodium ethoxide to yield ethyl  $\alpha$ -cyano- $\alpha$ -(3-methylcyclohexenyl)- $\beta$  phenylpropionate (I) which on cyclisation, followed by hydrolysis and dehydrogenation, furnishes 2-methylphenanthrene.

We needed 2-methylphenanthrene for our investigation on Friedel-Crafts' reaction (*Science & Culture*, 1947, 12, 410; 1948, 14, 40). Although various methods have been recorded in literature for its synthesis, the above compound was prepared following the method of Ganguli (*ibid.*, 1941-42, 7, 319) for the synthesis of phenanthrene derivatives.

Ethyl 3-methylcyclohexylidene-cyanoacetate was condensed with benzyl chloride in the presence of sodium ethoxide in ethanol solution according to the procedure of Cope *et al.* (*J. Amer. Chem. Soc.*, 1938, 60, 2903) to yield ethyl  $\alpha$ -cyano- $\alpha$ -(3-methylcyclohexenyl)- $\beta$  phenylpropionate (I) as a viscous liquid.



The cyclisation of (I) was effected with concentrated sulphuric acid and the cyclised product was hydrolysed *in situ* by the addition of aqueous acetic acid (1:1) and refluxing for thirty five hours. A gummy acid was isolated which did not decolorise bromine in carbon tetrachloride solution and was converted into its methyl ester by

\* National Council of Education Research Scholar.

refluxing with methanol and concentrated sulphuric acid. Hydrolysis of the above ester did not yield any crystalline acid, and other means to induce crystallisation also failed. It is possible that the gum represents a mixture of structural (IIa, III) and steric isomers. However, the acid could be converted into its anilide and a homogeneous product of m.p.  $199^{\circ}$  was isolated in 58% yield.

The gummy acid was then dehydrogenated with selenium without further purification and the resulting product was directly converted into its picrate; on crystallisation from methanol (five times) the product melted at  $117-118.5^{\circ}$  (Haworth, *J. Chem. Soc.*, 1932, 1123, records m.p.  $118-119^{\circ}$ ).

2-Methylphenanthrene (IV) was isolated from the above picrate by treatment with dilute ammonia solution, which after crystallisation from 95% ethyl alcohol melted alone or mixed with an authentic specimen at  $55^{\circ}$ .

The formation of a homogeneous anilide in fairly good yield and isolation of only 2-methylphenanthrene from the dehydrogenation experiment indicate that (IIa) represents the major portion of the product obtained on ring-closure and hydrolysis.

#### EXPERIMENTAL

*Ethyl  $\alpha$ -Cyano- $\alpha$ -(3-methylcyclohexenyl)- $\beta$ -phenylpropionate* (I).—Ethyl 3-methylcyclohexylidene-cyanoacetate (64.5 g.) after cooling for half an hour in an ice and salt bath was added to a sodium ethoxide solution (from 7.3 g. of sodium and 225 c.c. of dry ethanol), also cooled for the same period in a similar manner. The mixture thus obtained was cooled for further 45 minutes with occasional shaking. Benzyl chloride (42 g.) was then added to it and the reaction mixture was immediately transferred on a boiling water-bath and refluxed for 6 hours. The reaction mixture was cooled, diluted with water and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulphate, the ether was removed and the product was distilled in vacuum, b.p.  $185^{\circ}/3$  mm., yield 80 g. (86%). (Found: N, 4.86.  $C_{19}H_{23}O_2N$  requires N, 4.71 per cent).

2-Methylphenanthrene (IV).—Cold concentrated sulphuric acid (48 c.c.) was added to the above ester (30 g.) cooled in iced water. The reaction mixture was allowed to stand for 12 hours and then refluxed for 35 hours with the addition of glacial acetic acid (72 c.c.) and water (72 c.c.). Water was added and the mixture was extracted thoroughly with ether. The acidic material was isolated by washing the ethereal solution with dilute sodium bicarbonate solution, followed by acidification. The crude gummy material was esterified with methanol (100 c.c.) and concentrated sulphuric acid (d 1.84, 6 c.c.) by refluxing for 18 hours. The product was worked up by dilution with iced water and extraction with ether. The ether extract was washed with water, dilute sodium carbonate solution and water successively and dried over anhydrous sodium sulphate. After removing the ether, the residue was distilled in vacuum, b.p.  $180^{\circ}/6$  mm., yield 8 g. (Found: C, 78.89; H, 8.59.  $C_{17}H_{14}$  requires C, 79.07; H, 8.52 per cent).

The above ester (6 g.) was hydrolysed by refluxing with caustic potash (3 g.) in methanol (26 c.c.) for 4 hours. After removal of the methanol the residue was dissolved in water and the neutral matter was extracted with ether. The aqueous solution was

acidified with dilute hydrochloric acid and the gummy acid was extracted with ether. From the ether solution the acid was extracted with dilute sodium bicarbonate solution and was obtained again as a gum on re-acidification. The product was then purified by distillation in vacuum, b.p.  $210^{\circ}/4$  mm., yield 4 g.

*Preparation of the Anilide.*—Thionyl chloride (1.2 c.c.) and one drop of pyridine were added to a solution of the above acid (2 g.) in dry ether (10 c.c.), cooled in ice water and left as such for 2 hours with occasional swirling. Ether and excess of thionyl chloride were removed under diminished pressure at  $55^{\circ}$ - $60^{\circ}$ . The viscous residue was dissolved in thiophene-free benzene (10 c.c.) and cooled in ice water and to it was added slowly a solution of aniline (4 g.) in chloroform (25 c.c.). The reaction mixture was treated with water and the organic layer separated and thoroughly washed with water. Solvents were removed and the anilide was obtained as a crystalline residue. Crystallisation from petroleum ether and then from methanol yielded a product of constant m.p.  $199^{\circ}$ , yield 1.5 g. (58% of the theory). (Found: N, 4.94.  $C_{22}H_{20}ON$  requires N, 4.4 per cent).

The above acid (2 g.), purified by distillation, and selenium (8 g.) were heated in a metal-bath at  $290^{\circ}$ - $300^{\circ}$  for 24 hours and then at  $300^{\circ}$ - $315^{\circ}$  for another 24 hours. The product was extracted with benzene, filtered from excess of selenium and dried. After removal of the benzene the residue was heated with a little sodium at  $150^{\circ}$ - $160^{\circ}$  for 15 minutes.

The mixture was cooled, extracted with benzene and the residue distilled after removal of the solvent. The oily distillate was converted into its picrate by treating with a saturated solution of picric acid in ethanol. The picrate after several crystallisations (five times) from methanol was collected as orange-yellow crystals, which melted at  $117$ - $118.5^{\circ}$  (mixed m.p. with picric acid, m.p.  $121^{\circ}$ , was checked and a depression was observed).

2-Methylphenanthrene was regenerated from the picrate with dilute ammonia solution and was purified by crystallisation from 95% ethyl alcohol, m.p.  $55^{\circ}$ . The mixed melting point with an authentic specimen of 2-methylphenanthrene showed no depression.

## ADSORPTION OF ALCOHOL ON SILICA GEL

BY B. P. GYANI

The effects of ageing and different temperatures of evacuation on silica gel have been studied in respect of adsorption of anhydrous alcohol. There was little change in adsorption isotherms as long as the temperature of evacuation did not exceed a certain limit. Beyond this the adsorption improved at all pressures for the samples of gel used. Ageing improved adsorption at higher pressures but depressed it at lower ones. A fresh gel did not show hysteresis unless the temperature of evacuation was about 300°. Older gels or those evacuated at higher temperatures showed permanent hysteresis in adsorption, but the hysteresis region was not alike for different samples of the gel. About 2% of the adsorbed liquid could not be pumped out even at elevated temperatures. The gel had sometimes to be flushed a number of times to obtain reproducible adsorption branches.

In a previous communication (*J. Phys. Chem.*, 1945, 49, 226) the author has studied the adsorption of methyl, ethyl, *n*-propyl and *n*-butyl alcohol on silica gel. The adsorption isotherms plotted as the amount adsorbed per g. of the gel, ( $x/m$ ), against the pressures of the vapours, were found to possess a feature which did not appear with some other vapours such as hydrocarbons, esters and ketones (*Proc. Nat. Acad. Sci. India*, 1944, 14, 85). These isotherms of alcohols appeared to consist of several loops whereas in other cases they were more or less smooth. It was therefore decided to study the adsorption of at least ethyl alcohol in fuller detail, working with a fresh sample of silica gel and with the alcohol purified and dehydrated with greater care than before.

### EXPERIMENTAL

A sample of silica gel was prepared in large quantity. Commercial sodium silicate syrup was thinned down with water and diluted to a density of 1.12. Commercial hydrochloric acid was diluted to a density of 1.05. Equal quantities of the two solutions, 30-35 c.c. each, were then mixed with vigorous shaking in a large boiling tube. The clear solution, slightly yellowish due to the presence of iron, was collected in shallow porcelain basins and allowed to gelate at room temperature. After three or four days, when it had set to a stiff gel, it was cut into small pieces, washed with distilled water to remove most of the electrolytes, and then heated on a water-bath with intermittent changes of water for another 2 or 3 days. This operation eliminated all the remaining impurities in the gel while at the same time permitting it to age at about 70°-80°. The gel, a little shrunken in size, was now in the form of perfectly transparent, colorless lumps. It was desiccated in a porcelain basin over the water-bath. The lumps were now greatly reduced



in size and the material became hard and brittle. It was then transferred to a muffle furnace and kept at 350°-400° for 3 hours. On cooling, it was stored in a bottle over phosphorus pentoxide. This sample of the gel is described as the "UCL gel".

Another sample of the gel on which the earlier measurements had been carried out (Gyani, Thesis, Patna University, 1944, p. 99 *et seq*) was also used for comparison. It had been prepared in the same way as described above except that the gelation had taken place at a higher temperature, and the final desiccation was done on a sand-bath at 300°-350° in a current of dry air. This sample is called the "Patna gel".

The commercial absolute alcohol was kept in contact with some highly desiccated silica gel to remove any strongly adsorbable impurities. It was then stored overnight over freshly ignited quicklime. The final dehydration was done over aluminium-mercury couple after which the liquid was fractionated (b.p. 78.5° at 767.15 mm., s.p. gr., 0.791 at 18°, vapour pressure at 35°, 101 mm).

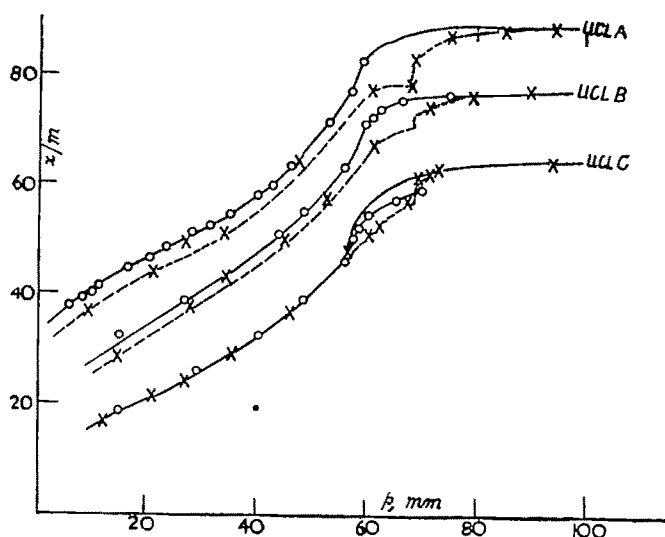
The adsorption apparatus used was similar to those described previously (*loc. cit.*). The amount of adsorption at a given pressure was determined by observing the increase in the weight of a bulb containing a known amount of the adsorbent. A liquid trap, cooled in solid carbon dioxide, effectively prevented any vapour from entering the pump in the new apparatus. As before, the experiments were carried out at 35° by enclosing the entire apparatus in a thermostat. The pressures were read on a metre scale rigidly attached to the mercury manometer with the help of a telescope placed 4' away. The error due to changes of level in the reservoir of mercury was small, about 0.5 mm. for 100 mm. change in pressure. The fractional error being constant had simply the effect of shortening the unit itself by about 0.5% and was consequently neglected. One can see that in the present method every single observation is absolute and not affected by accumulated errors from previous measurements to which the volumetric methods are open. It is significant that in these measurements reproducibility is good, even in the region of saturation where Coolidge (*J. Amer. Chem. Soc.*, 1924, 46, 603) found unsatisfactory results. Further, experiments in adsorption and desorption are carried out with equal ease and accuracy.

In the earlier measurements at Patna (Thesis, Patna University, *loc. cit.*) the gel had been freshly prepared and was evacuated at about 250°. The heating was done by a Bunsen flame, the bulb having been wrapped in a few folds of asbestos paper. The adsorption and desorption isotherms were found to coincide in these measurements with this gel, that is to say, no hysteresis was detected. When the experiment was repeated in London with the fresh UCL gel, evacuated at a higher temperature, a large-hysteresis appeared prior to saturation. The temperature of activation, the mode and duration of heating

and the age of the gel might each be playing a part in the appearance of hysteresis. It was therefore decided to take measurements with both the UCL gel and the Patna gel, which was now about two years old, after a final evacuation at different temperatures. The UCL gel was heated in different experiments both by a Bunsen flame and by enclosing it in an electrically heated oven whereby a more uniform temperature could be attained. Some of the results of these measurements are shown diagrammatically in the accompanying figures. The amounts of adsorption,  $x/m$ , are expressed in g. mol. of the liquid per g. of gel  $\times 10^{-4}$ . The pressures are in mm. of mercury. The different treatments of the gel prior to adsorption measurements are denoted by capital letters. These treatments are recorded in Table I.

The results of adsorption measurements with the UCL gels A, B, C, each of which had been heated in a flame during evacuation are shown in Fig. 1. The isotherm for the gel UCL-B has been shifted along the adsorption axis by  $10 \times 10^{-4}$  mol. per g. from that for the gel A for the sake of clarity. The isotherm for C has been similarly shifted with respect to that for B. The adsorption is quite large even for the smallest pressures recorded.

FIG. 1

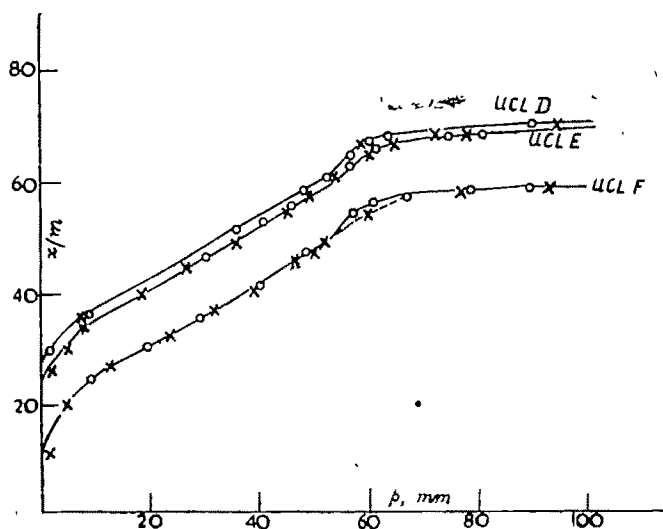


For the gel UCL-A and -B the adsorption curve denoted by crosses and dotted lines lies considerably below the desorption curve denoted by circles and full lines. The difference is less for the gel B which was heated for the second time, and vanishes with the gel C which was heated for the third time. It is likely that this difference between the adsorption and desorption isotherms was due to imperfect flushing of the gel. The difference between the adsorption and desorption isotherms in the pressure range of 55-75 mm. was large and

remained as such during successive heatings of the gel. In other words, a permanent hysteresis region existed at these pressures. It can be observed that the shapes and locations of the isotherms are substantially retained during the successive heatings at the same temperature.

Some of the results of measurements on the cold, evacuated UCL gel D and the gels E and F, evacuated under uniform electrical heating, are shown graphically in Fig. 2. The first few measurements with D were very erratic on the adsorption side but the adsorption curve gradually settled down in the close neighbourhood of the first desorption curve after many flushings of the gel with vapour. The adsorption and desorption points occurred close together for the gels E and F and could be represented by the same curves in the case of each gel. As a matter of fact, the three isotherms almost overlap each other so that to obtain clarity the isotherm for E has been shifted  $10 \times 10^{-4}$  mol. per g. downwards along the  $x/m$  axis. There is no evidence for any permanent hysteresis for the gels D and E, but a small one could be detected for the gel F in the pressure region 52-67 mm.

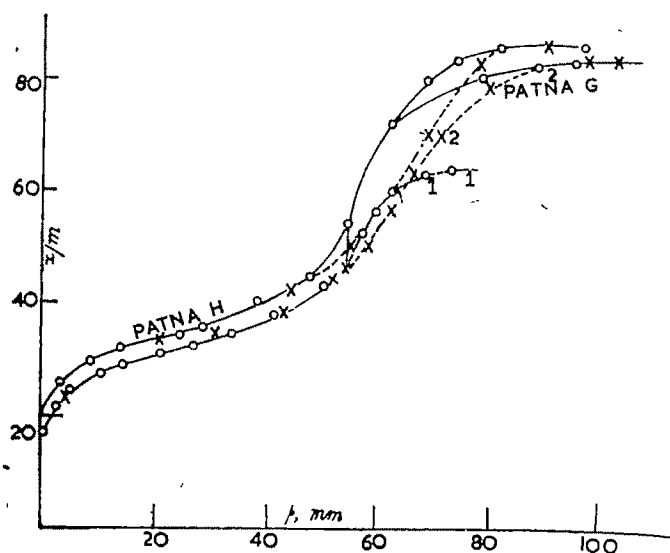
FIG. 2



The isotherms obtained with the gels Patna G, cold evacuated, and Patna H, evacuated at  $320^\circ$  under uniform electrical heating, are shown in Fig. 3. These graphs are similar to those for the gels UCL-A, B or C. Hysteresis occurs with each gel and extends over a large pressure range, viz. 50-80 mm. Both the adsorption and desorption isotherms in this region are steeper than the corresponding ones for the UCL gels.

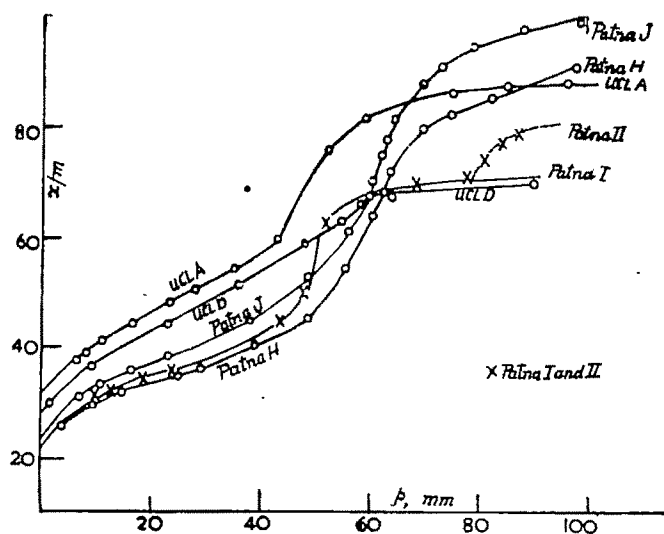
The isotherms described above obviously belong to three distinct groups. The first consists of the gels UCL-A, B and C. The second comprises the gels UCL-D, E and F and the third, the Patna gels, G and H. For the sake of comparison representative isotherms of each group are reproduced in Fig. 4. The isotherms of three additional gels, Patna I and II and Patna J, whose

FIG. 3



adsorptions had been determined at an earlier date at Patna, are also included in this diagram. It is found that all the Patna gels form a bunch by

FIG. 4



themselves towards the lower pressures and so do the UCL gels. The latter show about 10% better adsorption in this region.

*Effect of Temperature of Evacuation*

One can see from Fig. 4 that the maximum amount of adsorption, *i.e.* the adsorption attained at the highest pressures, may differ greatly for different samples of the gel. The values of maximum adsorption are conveniently summarised in Table I.

TABLE I

Description of the gel.	Age.	Mode of heating.	Temperature of evacuation.	Max. adsorption (g. mol. per g. gel $\times 10^4$ ).
Patna J.	2 years	Flame	Over 450°	101
Patna H	3 "	Electrical	320°	88-91
Patna G	3 "	No heating	30°	83-84
UCL-A, B	1 month	Flame	Over 450°	88
UCL-C	2 "	"	Over 450°	84
UCL-D	3 "	No heating	30°	70
UCL-E, F	3 "	Electrical	200, 300°	69
Patna I	Some "	Flame	About 300°	70
Patna II	Some "	"	About 400°	79

The effect of temperature of evacuation on adsorption can be clearly observed by comparing the maximum amounts of adsorption attained by gels of comparable ages. Among the Patna gels the best adsorption is shown by the gel J which was evacuated at the highest temperature. The value of maximum adsorption for the cold evacuated gel Patna G increased from 83-84 units to 88-91 when the temperature of evacuation was increased to 320°. Although the gels UCL-D, E, F were evacuated at quite different temperatures, the saturation values remained practically constant at 69-70 units. But when the temperature of evacuation was raised to over 450°, *e.g.*, in the case of the gel UCL-A, the value came up to 88, an increase of over 25%.

A curious isotherm was given by the gel Patna II. Up to a pressure of 60 mm. the graph coincided entirely with the Patna I isotherm. The two were satisfactorily reversible in this region and there was no evidence of hysteresis. When the gel Patna I was heated to a higher temperature to obtain the gel Patna II, a new portion of the adsorption isotherm appeared near the saturation pressure. By an oversight the desorption curve between 80 and 60 mm. was not mapped, but by comparison with the gel UCL-A, which gives a similar graph, it is probable that hysteresis existed and the author's earlier statement (*J. Phys. Chem.*, 1945, 49, 226) requires correction. In this connection it is interesting to note that the upper part of the alcohol isotherm on the gel Patna G was again missed in the first few adsorption measurements. The graph came to an end along the dotted line marked 1 in Fig. 3. After several flushings of the gel with vapour the adsorption isotherm rose up as

shown by the dotted line marked 2 and remained constant there. The anomalous behaviour noted in these experiments recalls some earlier observations such as those of McBain ("The Sorption of Gases and Vapours by Solids", p. 94, G. Routledge and Sons, Ltd., London, 1932).

Recalling the observations already recorded, it is easy to see that the temperature of evacuation plays an important part in determining the occurrence of hysteresis. Thus, among the fresh UCL gels, permanent hysteresis was not observed as long as the temperature of evacuation was below 300° (the gels D and E). At 320° the hysteresis appeared but was quite small in size (the gel F). When the temperature of evacuation was increased to about 450°, the region of hysteresis became large. A similar effect probably took place with the gels Patna I and II as just described.

The observations show that the hysteresis in the adsorption of alcohol by fresh samples of silica gel appears only when the gel has been evacuated well over 300°. This factor might explain the absence of hysteresis from the isotherms of water on silica gel obtained by Patrick, Davis, and Barclay ("Colloid Symposium Annual", 7, p. 130, Johns Hopkins, 1929). Patrick evacuated his gel at 350°. Probably a higher temperature of evacuation for his particular gel might have brought out hysteresis.

#### *Effect of Ageing*

It is observed from these experiments that the age of the gels plays an important part in determining the amount of adsorption and its variation with pressure. The effect of increasing age is often similar to that of increasing temperature of evacuation. For instance, both of them produce a rounding off of the isotherm towards higher pressures so that it merges gradually into the saturation portion (cf. Patna I and Patna J, or UCL-D and UCL-A, Fig. 4).

Increase in age probably depresses the amount of adsorption in the region of lower pressures (cf. Patna J and Patna H, Fig. 4), but definitely increases it in the region of higher pressures. This fact is clearly brought out by comparing values of maximum adsorption for the gels UCL-D, E, and F, which, in spite of evacuation at different temperatures remains constant at 69-70 g. mol.  $\times 10^{-4}$  per g. of the gel. If a similar rule held for the gels Patna I and G we have to conclude that the increase in the value of the maximum adsorption from 70 to 84 units is due to the ageing of the gel. Manegold (*Kolloid Z.*, 1939, 81, 19) quotes that three samples of silica gel due to van Bemmelen had pore volumes 0.410, 0.485, and 0.570 when fresh, six months old and five years old respectively. The figures correspond with an increase in adsorption of over 15% in six months and over 35% in five years, whereas the Patna gel under discussion shows a total increase of about 20% in 3 years. Holmes and Elder (*J. Phys. Chem.*, 1931, 35, 82) have observed a decrease in pore volume in contrast to these results with increasing age for eleven samples of silica gel.

The present observations also tend to show that the temperature of evacuation is not the only factor which determines hysteresis. A large hysteresis region occurs with the gel Patna G which was evacuated only at room temperature. So, the occurrence of hysteresis in this case must be ascribed to the ageing alone. The shapes of the hysteresis region for the aged Patna gels and the fresh UCL gels differ and so do their sizes. It appears that these differences are again due to ageing, noting the fact that if hysteresis did exist with the gel Patna II, its shape must have been similar to that for the gel UCL-A.

### *Changes in the Gel Structure*

It is generally considered at present that the internal structure of silica gel consists of a conglomeration of small particles or micelles of the gel material partly coalescing with each other and partly separated by empty capillary spaces which may normally contain air and water. These capillary spaces may be anything in dimensions between sub-microscopic and molecular. The same is true about the micelles. The fact that a piece of raw silica gel shrinks greatly in size on progressive drying though retaining its transparency shows that these dimensions must undergo changes according to circumstances. Gels with such structures are potentially capable of both surface adsorption and capillary condensation.

Sigmoid adsorption isotherms, such as the ones obtained in these experiments, are usually considered to involve mainly surface adsorption at lower pressures and mainly capillary condensation at higher pressures. The Brunauer-Emmett-Teller theory (Brunauer, "Adsorption of Gases and Vapours", p 140, Oxford University Press, 1944) seeks to unify these two processes in a single expression for the amount of adsorption. These workers consider that the lower parabolic part of such isotherms ("point B") marks the completion of a unimolecular layer of adsorbed molecules so that if the amount of adsorption corresponding to this point is determined one can have a measure of the internal area of the adsorbent.

The observations recorded above, as far as they go, tend towards the the following conclusions :

(1) Evacuating above certain temperatures (depending upon different gels) improves adsorption at all pressures (cf. Table I and the isotherms of UCL-D and A or Patna G, H, and J).

(2) Ageing improves adsorption at higher pressures but depresses it at lower pressures (cf. isotherms of Patna I and Patna H).

(3) Evacuation above a certain temperature may produce hysteresis (cf. isotherms of UCL-D, E and A, B, C, F or Patna I and II).

(4) Ageing beyond a certain limit appears to produce a similar effect (cf. isotherms of Patna I and G, H).

It appears to the author that these observations may be explained if one considers that evacuating above certain temperatures brings about shrinkage of individual micelles. The shrinkage would be accompanied by a general diminution in the area of individual micelles, but if the shrinkage is considerable, as it should be if temperatures are high, the areas of contact between the micelles may open up, thus increasing the total surface. Continued heating at low temperatures may not only shrink the micelles but probably smooths out the roughness on the surface by a process of sintering of the protuberances. Ageing may produce similar effects. Hence, under these conditions there would be a small diminution of adsorption corresponding to "point B" as is observed in these experiments. Conditions bringing about shrinkage and sintering will naturally increase the capillary volume of the adsorbent, so that elevated temperatures of evacuation or ageing should produce an increase in the capillary adsorption, as has been noted above.

It further appears to the author that a certain minimum width of capillaries is necessary before hysteresis may appear. To produce wide capillaries prolonged ageing or evacuation at elevated temperatures would be necessary which appears to explain in a simple way the last two observations recorded above.

Another important observation from these experiments was that about 2% of the adsorbed alcohol was irreversibly retained by the gel and it could not be pumped out into the best vacuum available at the highest temperatures employed in these experiments. The gel became distinctly coloured after a prolonged series of runs although no products of the decomposition of alcohol could be detected by ordinary analytical methods. This irreversible retention of the adsorbed liquid agrees with many previous observations (McBain, "Sorption", p. 94; Brunauer, *loc cit.*, p. 419). It appears that a portion of the alcohol is adsorbed on active points in the gel structure as considered in a previous paper by the author (*J. Phys. Chem.*, 1945, 49, 442).

Part of this work has appeared in the author's thesis for the Ph. D. degree, London 1947. The author is grateful to Professor S. Sugden and the authorities of the University College, London for providing all facilities for the experimental work and to the Patna University for the award of a Birla scholarship.

DEPARTMENT OF CHEMISTRY,  
SCIENCE COLLEGE,  
PATNA 5.

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## STUDIES ON RANCIDITY OF BUTTERFAT. PART V. THE EFFECT OF TEMPERATURE

BY S. MUKHERJEE

The induction period of the fat diminishes with temperature, peroxide value increasing with time; at the high temperatures, viz., 105° and 120°, there is enhanced decomposition of the peroxides.

Temperature as a means of speeding up chemical reactions needs no introduction and in common with all other chemical reactions, the rate of development of rancidity in a fat sample exposed to air is increased by raising the temperature. However, it has not been known whether an elevation of temperature would result in a simple, regular and uniform increase in the rate of the reaction. It has been the purpose of this communication to study whether oxidation of butterfat in absence of light and positive catalyst has a normal temperature coefficient. The rate of development of rancidity has been studied at 60°, 85°, 105° and 120° respectively. For this purpose 20 c.c. samples of butterfat were placed in flat glass petri dishes (3" dia.) and were incubated in electrically controlled air-oven. At desired intervals one dish was taken out and peroxide and Kreis measurements were immediately made or as in some cases, the sample was stored in the refrigerator immediately and determinations were made next day. The experimental results are tabulated below.

TABLE I

*Kreis and peroxide values of butterfat oxidised at diff. temp.*

Temp.=60°.										
Exposure (hrs.)	1	2	4	5	8	10	12	15	18	20
Kreis No.	0.2	0.5	0.7	1.0	1.2	1.5	1.7	2.0	3.8	5.0
Peroxide value	0.5	1.0	1.3	2.0	3.7	5.0	7.5	9.0	12.5	20
Temp.=85°.										
Exposure (hrs.)	1	2	4	5	6	8	9	11	12	14
Kreis No.	0.5	1.0	1.1	1.4	1.5	1.6	1.6	1.7	2.0	2.0
Peroxide value	0.65	1.2	2.4	3.1	4.0	6.0	7.6	12.0	14.0	1.0
Temp.=105°.										
Exposure (hrs.)	1	2	4	5	6	8	10	12		
Kreis No.	1.0	1.1	1.4	2.2	5.3	7.1	16	19.8		
Peroxide value	1.25	3.0	10.0	13.85	18.0	33.5	80.0*	50.0		
Temp.=120°.										
Exposure (hrs.)	0.5	1	3	5	7	8	9	10		
Kreis No.	1.3	4.7	5.1	7.7	10.4	17.2	17.7	20		
Peroxide value	2.0	4.54	32.5	52.0	115.0*	67.5	62.5	50		

\* After this point peroxide decomposition starts.

The peroxide and Kreis values were determined by the methods described previously (this *Journal*, 1950, 27, 551).

The rate of development of rancidity at different temperatures is shown graphically in Figures 1-4. It appears from these data that the rate of forma-

FIG. 1

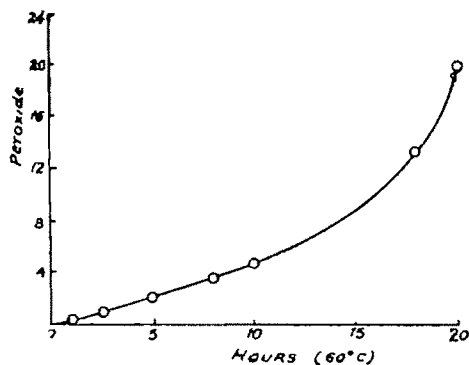
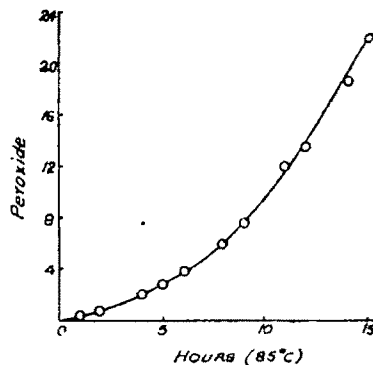


FIG. 2



tion of peroxide steadily increases as the temperature is raised up to 85°, the duration of induction period (taken as the time necessary to reach a peroxide value of 2.0) gradually diminishes. Further increase of temperature causes rapid formation of peroxides, and autoxidation of the fat seems to proceed

FIG. 3

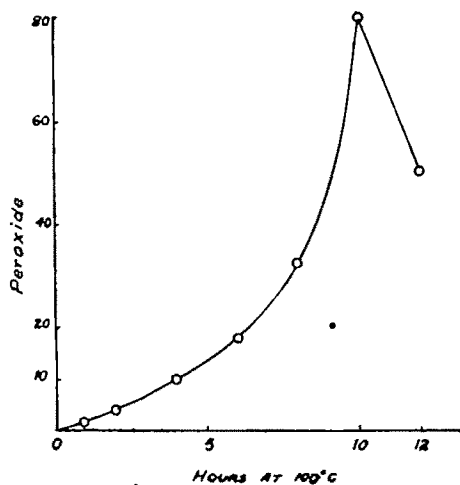
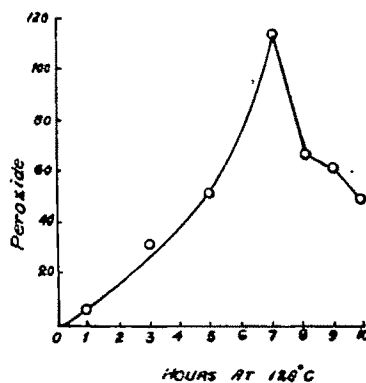


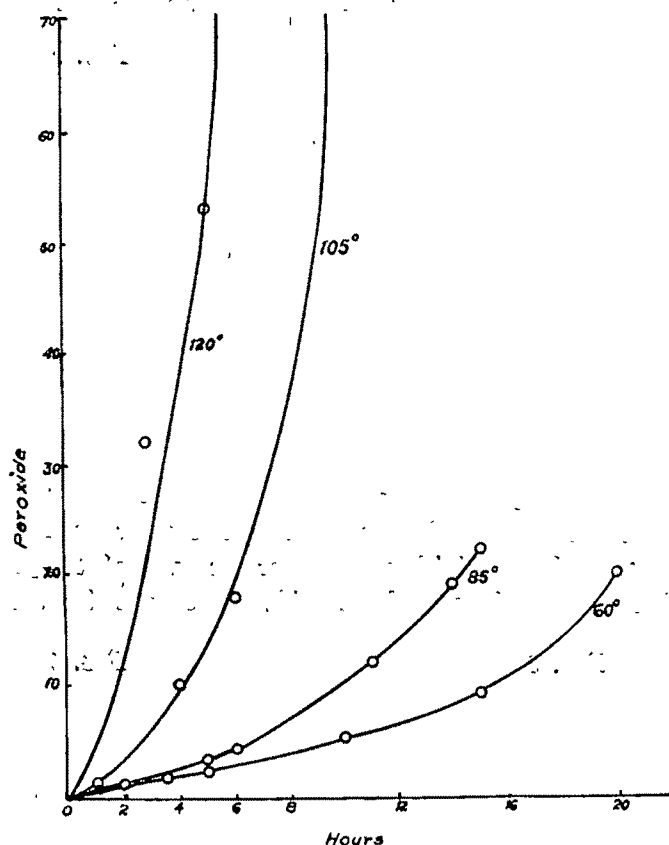
FIG. 4



with little or practically no induction period at temperatures above 100°. Figure 5 shows the peroxide curves at various temperatures on the same abscissa of time and demonstrates more clearly the difference due to temperature. The steepness of the curve steadily increases as the temperature is increased. At higher temperatures decomposition of peroxide also plays an important role as can be seen from Figures 3 and 4. The time to reach a

definite peroxide value (viz. 2.0) progressively diminishes as the temperature is increased and this is illustrated in Table II together with the temperature

FIG. 5



coefficients, calculated between various temperature ranges.

TABLE II

*Induction period of butterfat at various temperatures.*

Temp. ...	...	...	37°	60°	85°	105°	120°
Induction period (hrs.)	...	...	1080	5	3	1.5	0.75

TABLE III

*Temperature coefficient.*

Temp. range ...	...	...	60°—85°	85°—105°	105°—120°
Temp. coeff. ...	...	...	1.65	2.0	2.0

It appears that the induction period of the fat diminishes progressively with the rise of temperature, and the speed of decomposition of peroxides becomes progressively greater as increased oxidation progresses at higher temperatures viz. at 105° and 120°.

DEPARTMENT OF APPLIED CHEMISTRY,  
UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA.

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## STUDIES ON RANCIDITY OF BUTTERFAT. PART VI.

### THE ACTION OF LIGHT

BY S. MUKHERJEE

Butterfat, exposed to diffused light, light from a tungsten filament lamp, ultraviolet light and X-rays, develops rancidity in presence of oxygen, the rate of development of rancidity being proportional to the intensity of the exciting source. In complete absence of oxygen even X-rays and ultraviolet light are ineffective in producing off-flavour. Only the lower saturated acids,  $C_4$  and  $C_6$ , are oxidised by the action of light, the higher members remaining unaffected.

It has long been known that fats and fat containing food materials exposed to sunlight develop an unpleasant odour and flavour much more rapidly than when preserved in the dark. Ritsert (*Natures. Wchnschhr.*, 331, 343) observed that exposure to light had a remarkable effect in accelerating the development of rancidity. But subsequent reports show a great deal of confusion regarding the part played by light, some asserting that light and oxygen are both essential for the onset of rancidity, while others claim that light alone in absence of oxygen is capable of producing rancidity (Wagner *et al.*, *Z. natur. Nahr. Genussm.*, 1913, 25, 704). Schmalfuss and collaborators (*Marg. Ind.*, 1935, 25, 215) have shown that saturated and unsaturated fatty acids and glycerides give rise to small amounts of odorous aldehydes and ketones when subjected to prolonged heating or exposed to ultraviolet light. These workers assert that oxygen and moisture are not essential but assist the reaction and that ketones and acids are produced during irradiation more easily from those containing 12 or fewer carbon atoms than from  $C_{14}$ ,  $C_{16}$  and  $C_{18}$  acids. It is a common knowledge that ultraviolet light is very effective in accelerating the deterioration of fats. It has been shown by Lea (*Proc. Roy. Soc.*, 1931, 108, B, 175) that a fat exposed at a constant room temperature to the light from an electric lamp oxidises much more rapidly than a control sample in the dark, in spite of the fact that the ultraviolet component of the radiation from the electric lamp filament is very small.

Comparatively little work has been done on the quantitative relationship between rancidity and intensity of illumination. Rogers and Taylor (*J. Phys. Chem.*, 1926, 30, 1334) studied the absorption of oxygen by linseed oil under ultraviolet irradiation and were able to show that the spoilage, which was negligible in the absence of light, was not directly proportional to the intensity of illumination, but that weaker the light employed, the greater was the efficiency in producing rancidity.

It has already been shown (this *Journal*, 1947, 24, 239) that the role of light is one of positive catalyst and that samples of butterfat stored in diffused day light in the absence of oxygen fail to produce any organoleptic rancidity for the period studied. It may generally be accepted that the action of light consists in

accelerating rancidity and that irradiation in complete absence of oxygen is incapable of producing rancidity. The fact that apparently sweet fats sometimes become rancid when exposed to light, out of contact with air, has been explained by Lea (*loc. cit.*) as due to the presence in the fat of minute amounts of oxygen either in solution or in loose chemical combination with unsaturated acids. This oxygen under the influence of strong light may be quite sufficient to affect the flavour of fats.

With an idea to elucidating this point further, a detailed study has been made of the effect of light both in presence of oxygen as also in the complete absence of it, using different sources of illumination as the exciting agency, viz. sunlight, electric light from tungsten filament lamp, ultraviolet light from mercury vapour lamp and finally X-rays.

#### EXPERIMENTAL.

*Effect of Storage of Butterfat in Dark after Exposure to a 100-watt lamp for different Periods.*—Butterfat was placed in small petri dishes (3" diam.) and was irradiated for 1, 3, 5, 8, 10, 12 and 15 hours by light from a 100-watt tungsten filament lamp, the samples being kept at a distance of 15 cm. from the exciting source. After the desired period each sample was transferred to darkness at 37°. The development of rancidity was followed by the determination of the peroxide value and the results are tabulated below.

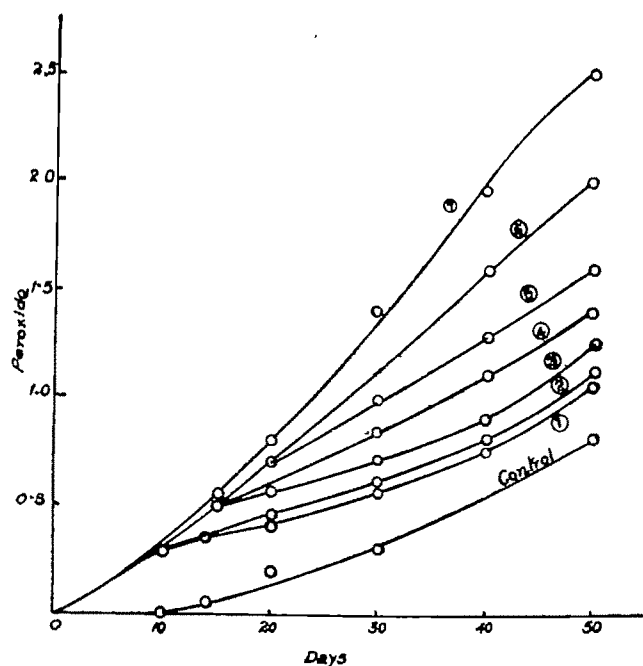
TABLE I

Expt. No.	Exposure.	Peroxide value after days.					
		10.	15.	20.	30.	40.	50.
1	1 hr.	0.25	0.35	0.40	0.55	0.75	1.05
2	3	0.25	0.35	0.45	0.60	0.85	1.20
3	5	0.25	0.50	0.55*	0.70	0.90	1.25
4	8	0.25	0.50	0.60	0.85	1.1	1.40
5	10	0.25	0.50	0.68	1.0	1.3	1.60
6	12	0.25	0.50	0.70	—	1.58	2.0
7	15	0.25	0.55	0.80	1.40	2.0	2.5
8	Control sample	0.0	0.05	0.20	0.30	0.55	0.80

Samples 1 and 2 developed slightly off-flavour. This was more pronounced in the case of samples 3-5. Samples 6 and 7 were distinctly rancid both organoleptically as well as from peroxide determinations. The control sample did not develop organoleptic rancidity until at the end of 60 days, when distinct signs of such rancidity could be detected.

It is evident from Table I that exposure to light of relatively low intensity even for a limited period can have a very pronounced effect on the development of oxidative rancidity on subsequent storage in darkness. The results are graphically shown in Figure 1 where oxidation can be seen to proceed in the absence of light at a rate depending probably on the amount of energy absorbed

FIG. 1



during the short exposure to light. From these results at least one thing appears certain that the increased oxidation in irradiated samples may be ascribed to the action of light, for under the experimental conditions the control unexposed sample did not develop detectable rancidity even at the end of one and a half month. Lea (*loc. cit.*) has studied a similar effect with a beef-kidney fat, and the present results are fully in agreement with those observed by him.

*Effect of Light Intensity.*—For this purpose, samples of butterfat were irradiated as before for a definite period (12 hours) at different distances from the exciting source (100-watt W-lamp) viz., 15 cm., 20 cm., 30 cm. and 60 cm. and the samples subsequently kept at atmospheric conditions at a temperature of 37° in an incubator. The results are shown in Table II.

TABLE II

Distance from lamp.	Peroxide value after days.			
	15.	20.	30.	45.
Control (unexposed)	0.14	0.30	0.40	2.4
15 cm.	0.60	1.00	3.7	5.9
20	0.60	1.00	3.5	5.0
30	0.40	0.82	3.0	4.0
60	0.30	0.50	2.4	3.0

It is evident from the above table that increasing the distance of the source of light from the fat *i.e.* decreasing the intensity of light, is also accompanied by a decrease in the development of peroxide value of fats, and it will not be wrong to conclude that the relation between the rate of oxidation and intensity of irradiation may be one of direct proportionality. Rogers and Taylor (*loc. cit.*), however, observed that in the oxidation of linseed oil, weaker the light employed, greater was the oxidation.

*Effect of Storage of Butterfat in Air on the Development of Rancidity after Exposure to Ultraviolet Light for different Periods.*—Samples of butterfat (50 c. c. each) were exposed to the action of ultraviolet light from a mercury vapour lamp in small dishes for 2, 5, 10, 15, 25, 35, 45 and 75 minutes respectively and after this period, the samples were removed to small open glass jars and kept stored in an incubator at 37.5°, after immediately determining the peroxide value of the fat samples. These were then analysed at suitable intervals and the experimental results are given in the table below.

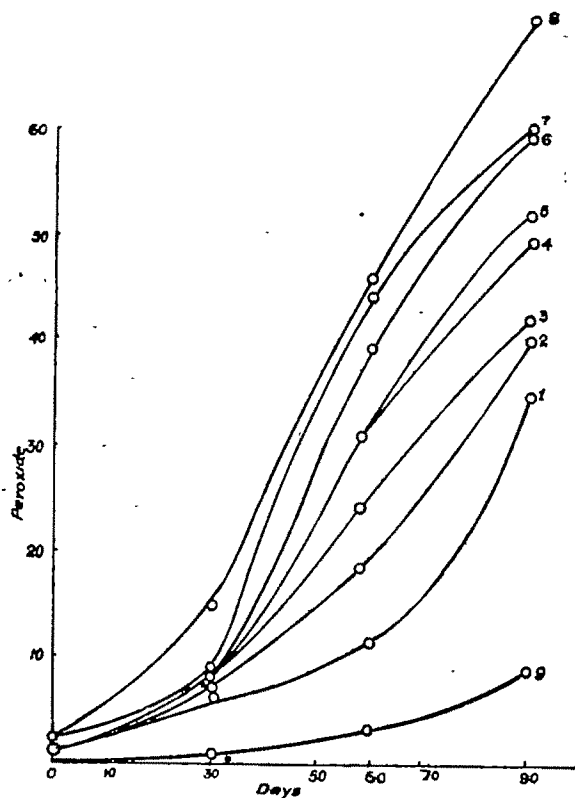
TABLE III

Both oxygen and moisture present ; storage temperature = 37.5°.

Expt. No.	Time of exposure.	Peroxide value					
		Original.	Immediately after exposure.	After 15 days.	After 30 days.	After 60 days.	After 90 days.
1	2 min.	0.56	0.86	2.7	6.8	11.5	35.4
2	5	0.56	1.0	3.0	7.2	18.7	40.1
3	10	0.56	1.0	3.6	8.0	24.1	42.3
4	15	0.56	1.30	3.8	8.1	31.4	49.5
5	25	0.56	1.30	3.9	8.1	31.1	52.0
6	35	0.56	1.45	4.0	8.0	39.0	59.2
7	45	0.56	1.72	5.3	10.0	42.5	60.6
8	75	0.56	2.10	5.6	15.0	49.5	70.0
9	Control	0.56	—	0.70	0.88	3.65	9.2

It will be clear from the above table that exposure of fats to ultraviolet light reduces the induction period considerably, pronounced rancidity being detectable at the end of 10 to 15 days. In samples 7 and 8, irradiated respectively for 45 and 75 minutes, the fats oxidised without induction period, off-flavours being detectable immediately after the exposure. The experimental results are shown graphically in Fig. 2.

FIG. 2



*Ultraviolet Irradiation and Rancidity in Presence and Absence of Oxygen.—*

So far the behaviour of light was studied in presence of atmospheric oxygen and pronounced oxidation was observed. In this section experiments were carried out to illustrate the function of light and oxygen on the development of rancidity. Ultraviolet light from a mercury vapour lamp was employed as the exciting source and samples of butterfat were irradiated at a distance of 15 cm. from the source in quartz vessels both in the presence and absence of oxygen. Complete absence of oxygen was effected by evacuation by means of



a diffusion pump for one hour only. Estimation of dissolved oxygen in the Van Slyke apparatus from a duplicate sample, evacuated for the same period, indicated completeness of the removal of oxygen. The time of exposure was 1, 2 and 24 hours.

TABLE IVA

Expt. No.	Condition of expt.	Time of exposure.	Values immediately after exposure		Organoleptic test.
			P.V.	Kreis.	
1	Oxygen present	1 hr.	0.86	2.2	Rancid, bad.
2	Do	2	0.90	2.6	" "
3	Do	24	4.50	10.0	Offensive
4	Oxygen absent	1	0.26	0.1	Practically unaltered
5	Do	2	0.28	0.1	Do
6	Do	24	0.26	0.1	Do
7	Control	...	0.26	0.1	Do

TABLE IVB

*Development of rancidity in the irradiated samples (Table IVA) when exposed to atmospheric conditions.*

Storage temperature = 37.5°.

Expt. No.	After 30 days.		After 60 days.		After 75 days.	
	P.V.	Kreis.	P.V.	Kreis.	P.V.	Kreis.
1	10.3	9.3	35.6	15.0	70.0	35.0
2	13.3	10.8	42.6	16.3	86.0	37.0
3	20.0	16.5	52.5	31.6	96.0	92.0
4	1.56	2.1	3.0	3.9	6.0	8.5
5	1.60	—	3.1	4.0	5.8	8.4
6	1.57	2.2	3.2	4.0	5.9	9.0
7	1.48	2.1	3.0	4.2	5.78	8.8

TABLE IVC

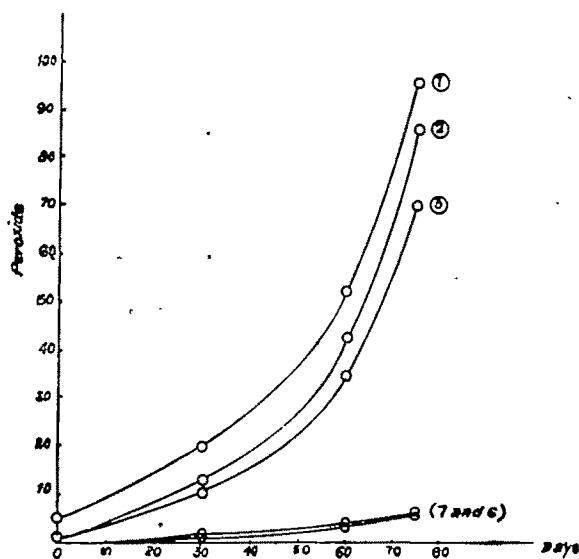
*Development of peroxide and Kreis values after 75 days in the samples irradiated in vacuum and stored as such.*

Hours of exposure.	After 75 days.		Organoleptic test.
	P.V.	Kreis.	
1	0.20	0.8	Smell unaltered
2	0.30	1.0	Do
24	0.30	1.2	Do
Control in air	5.78	8.8	Highly rancid
Control in vacuum	0.20	0.8	Not rancid

It will be evident from these tables that whereas exposure in presence of oxygen can produce off-flavour almost immediately after the exposure, the

smell remains unaltered after the period of exposure in absence of oxygen. Storage of the samples exposed subsequently to atmospheric conditions developed pronounced rancidity in samples 1, 2, and 3, where oxygen was present during irradiation, whereas samples 4, 5 and 6, irradiated in absence of oxygen oxidised very nearly at the same rate as the unexposed control sample (Table IVB). Duplicate samples exposed in complete absence of oxygen did not develop rancidity when stored as such even after the period mentioned

FIG. 3



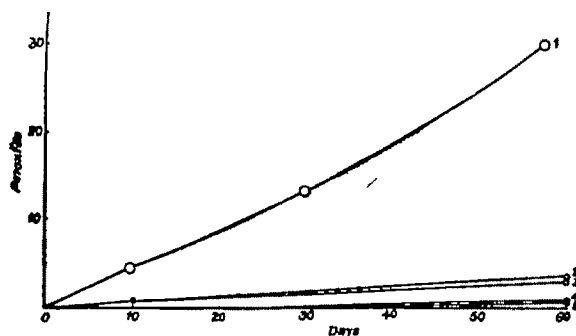
(Table IVc). Fig. 3 shows the behaviour of samples irradiated in ultraviolet in the development of rancidity in the presence and absence of  $O_2$ .

*Effect of X-ray Irradiation on the Development of Rancidity of Butterfat.*—

The experimental evidences assembled in the previous section clearly indicate that the part played by light consists definitely in accelerating the rate of autoxidation of fats by atmospheric oxygen and that rancidity cannot develop in the absence of oxygen even under the influence of ultraviolet irradiation. In this section the effect of X-rays, a more powerful source of radiant energy, has been used in the irradiation of fat and its effect on the development of rancidity has been studied in the presence and absence of oxygen. Thunberg's tubes were used for experiments conducted in absence of oxygen and the samples were exposed to the action of X-rays (wave-length  $2 \text{ \AA}$ ) for different periods of time, viz. 10 minutes, 15 minutes and 1 hour. The results in Table V show that exposure in the presence of oxygen for

10 minutes (No. 1) is sufficient to develop pronounced rancidity in butterfat, whereas the samples 2 to 4, which were irradiated in the absence of oxygen,

FIG. 4



oxidised as slowly as the control samples which had not been subjected to irradiation. This relationship is clearly shown in Fig. 4.

TABLE V

*Butterfat stored at 37.5°.*

Expt. No.	Condition of the experiment (moisture, 0.2%)	Original.	Immediately after exposure.	Peroxide value.		
				After 10 days.	After 30 days.	After 60 days.
1.	10 minutes' exposure in presence of oxygen	0.30	0.56	4.36	1.30	29.5
2.	10 minutes' exposure in vacuum and then kept exposed to atmospheric conditions	0.30	0.30	0.45	1.64	3.2
3.	15 minutes' exposure in vacuum and then exposed to atmospheric conditions.	0.30	0.30	0.40	1.54	3.3
4.	1 hour's exposure in vacuum and kept exposed to atmosphere	0.30	0.30	0.40	1.38	3.0
5.	15 minutes' exposure in vacuum and stored as such	0.30	—	—	—	0.52
6.	Control in light	0.30	—	—	1.48	3.0

These experiments strongly favour the view that oxygen is primarily essential for the onset of rancidity. Sample No. 5 stored in vacuum after 15 minutes' exposure to the X-ray irradiation practically underwent no change organoleptically, an observation which has also been made with the ultraviolet irradiation experiments in the previous section.

*Action of Light on the Oxidation of Saturated and Unsaturated Fatty Acids.*—The action of light has thus definitely been shown to consist in accelerating the rate of development of rancidity in fats and it is generally believed to affect the oxidation of the unsaturated constituents of the glyceride molecules. The possibility of decomposition of saturated fatty acid chain should not, however, be overlooked, particularly after the experiments of Schmalfuss *et al.* (*loc. cit.*) and hence it was considered necessary to study the behaviour of light on the oxidation of both the saturated and unsaturated fatty acids and their glycerides. All the saturated acids from butyric to stearic, and oleic and linoleic acids among the unsaturated acids were employed in this study; of the glycerides only tributyrin, tristearin and triolein were used. Ultraviolet light was used as the source of light in view of its pronounced accelerating effect, already observed. Ultraviolet irradiation in quartz test tubes for a period of 30 minutes was normally employed. In order to prevent any volatile products of oxidation escaping to the atmosphere, the quartz tubes were connected with short delivery tubes dipping under a small volume of water contained in a test tube. The oxidised acids or the glycerides as also the water containing any absorbed product of oxidation were subjected to tests for aldehydes by Schiff's reagent, peroxide test with KI and acetic acid and for ketones by salicylaldehyde reaction of Taufel and Thaler (*Chem. Zentr.*, 1932, I, 265). The following table summarises the results.

TABLE VI

*Effect of ultraviolet irradiation on fatty acid oxidation.*

	Peroxide test.	Schiff's test.	Salicylaldehyde reaction.
Butyric acid	—	+	—
Caproic acid	—	Very feeble	—
C <sub>8</sub> —C <sub>18</sub> acids (saturated)	—	—	—
Oleic acid	+	+	—
Linoleic acid	+	+	—
Tributyrin	—	+	—
Tristearin	—	—	—
Triolein	+	+	—

Even prolonged irradiation for 12 hours failed to develop aldehyde or ketonic substances with higher saturated acids. These results indicate that

the saturated fatty acids are not normally affected during the oxidation, and the action of light consists mainly in producing accelerated oxidation of the unsaturated glycerides only, with the formation of peroxidic compounds.

### C O N C L U S I O N

From the experiments enumerated above it is clear that light alone cannot be an initial starter of the rancidity in fats. As all these experiments have been conducted with samples, whose moisture content is 0.2%, one can also conclude with certainty that rancidity can be developed in the presence of oxygen alone, that light or moisture alone without oxygen cannot under any circumstances produce rancidity in fats. All previous observations, viz. Wagner *et al.* (*loc. cit.*) and Schmalfuss *et al.* (*loc. cit.*) upholding exposure to light as capable of producing rancidity in vacuo, and those of Godbole and Sadgopal (*Z. untersuch. Lebensmittel.*, 1936; 72, 35) claiming moisture as the fundamental cause of rancidity must therefore be erroneous. It has, however, been demonstrated in this paper that light plays a prominent role in producing accelerated rancidity in fats. Even exposure to weak artificial light is capable of decreasing the induction period of fats and can produce marked acceleration in the rate of subsequent oxidation, a conclusion already reached by Lea (*loc. cit.*). It is also clear that once a fat has been exposed to light rays so as to start oxidation at a sufficient rate, it cannot be stopped by removal of the exciting source. The nature and intensity of light also play a prominent role, ultraviolet light being more destructive than ordinary light and X-rays still more predominant in causing rancidity. From the results obtained, it may be concluded that at temperatures sufficiently low for thermal reactions to be negligible, fats exposed to strong illumination with free access of oxygen oxidise with little or no induction period at a rate which is roughly proportional to the intensity of light. The action of light consists essentially in accelerating the rate of oxidation of the unsaturated components of fats, but the lower saturated acids may be affected to a slight extent. Thus, exposure to light, though of undoubted importance, is only one of the factors which influence the development of oxidative rancidity.

The author acknowledges his indebtedness to Prof. M. N. Goswami for his valuable suggestions.

## 'FLUIDITY TEMPERATURE' OF SOME HOMOLOGOUS SERIES

BY ASOK KUMAR MUKHERJEE

The significance of  $T_s$ , the temperature of fluidity, has been brought out, and  $e^{\alpha T_s}$  has been shown to be equal to the ratio of the average volume of a molecule, which the molecule possesses when its fluid properties just appear, to the actual volume of the molecule. This has been established in the case of some homologous series from data available in the literature.

In a previous communication (this *Journal*, 1949, 26, 493) an equation relating fluidity ( $\phi$ ) of a liquid with its coefficient of thermal expansion ( $\alpha$ ) has been derived from considerations based upon Batschinski's equation (*Z. physikal. Chem.*, 1913, 84, 643) and also upon the assumption of the free volume in liquids as enunciated by Eyring (*J. Chem. Phys.*, 1936, 4, 283). This equation yields a linear plot of  $\phi$  against  $e^{\alpha T}$ , where  $T$  represents the relevant temperature and  $\alpha$ , the coefficient of expansion. The equation is of the form :

$$e^{\alpha T_s} + \frac{e^{\alpha T_s}}{C.V_s} \phi = e^{\alpha T} - a + b\phi \quad \dots \quad (1)$$

where  $a$  stands for  $e^{\alpha T_s}$  and  $b$ , for  $e^{\alpha T_s} / C.V_s$

In this derivation the concept of a temperature  $T_s$  has been introduced for the first time apparently for mathematical simplification. This particular temperature  $T_s$  represents the threshold temperature at which a liquid loses its free volume and becomes too compact to have any fluidity. This temperature therefore marks the limit from where the fluidity of any liquid starts and can thus be rightly designated as the "temperature of fluidity" for the particular substance.

It was also observed in the same communication (*loc. cit.*) that the straight lines obtained by plotting  $\phi$  against  $e^{\alpha T}$ , according to equation (1) above, converged to the same point on the  $e^{\alpha T}$ -axis for members of the same homologous series. As many as five different homologous series were reported therein and graphical representations of two of them shown. Another interesting feature which was noticed was that for all the series reported therein, the points of convergence were close to each other, being in the neighbourhood of  $e^{\alpha T_s} = 1.25$ . This striking feature, hit upon by chance, was suggestive of some important significance on the part of this particular temperature. In the present paper this aspect has been further developed and critically examined with reference to a few more homologous series and a theoretical interpretation attempted.

### EXPERIMENTAL

The cases of normal olefines and thiols-2 have been studied besides the cases of *n*-paraffins, *n*-alkylbenzenes, *n*-alkyl cyclohexanes, *n*-alkyl cyclo-

pentanes, and *n*-mercaptans, which have been reported in a preliminary manner in the earlier communication referred to above (*loc. cit.*). They are graphically

FIG. 1

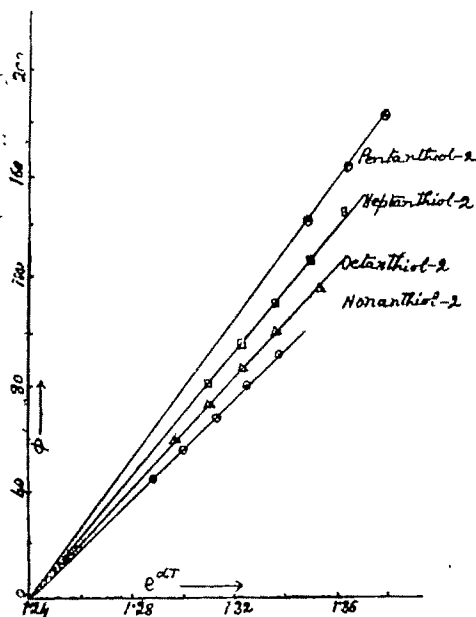
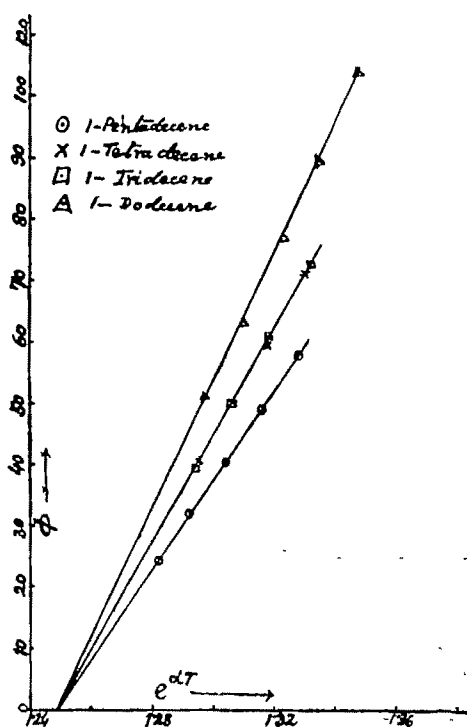


FIG. 2



shown in Figs. 1 and 2. The points of convergence on the  $e^{\alpha T}$ -axis, referred to as  $e^{\alpha T_s}$  have been summarised in the following table.

TABLE I

Homologous series.	Point of convergence on $e^{\alpha T}$ -axis ( $= e^{\alpha T_s}$ )
1. <i>n</i> -Paraffins	1.250
2. <i>n</i> -Alkylbenzenes	1.236
3. <i>n</i> -Alkyl cyclopentanes	1.252
4. <i>n</i> -Alkyl cyclohexanes	1.252
5. <i>n</i> -Mercaptans	
(a) Ethyl to butyl mercaptans	1.262
(b) Amyl mercaptan	1.250
(c) Hexyl to nonyl mercaptans	1.237
6. Olefines	1.250
7. Thiols-2(C <sub>8</sub> to C <sub>9</sub> )	1.240

The relevant data for the above hydrocarbons have been collected from the "Physical and Thermodynamic Properties of Hydrocarbons" published and very kindly supplied to us by the National Bureau of Standards, U.S.A. The data for *n*-mercaptans and thiols-2 have been taken from Landolt-Börnstein Tabellen. A cursory glance at the figures will impress that the values of  $e^{\alpha T}$  in the different cases are quite close to each other.

## DISCUSSION

### *Theoretical*

By definition the coefficient of thermal expansion of any substance is given by

$$\alpha = \left( \frac{d \ln V}{dT} \right)_P \quad \dots \quad \dots \quad \dots \quad (ii)$$

$$\text{whence } \ln \frac{V}{V_0} = \alpha T \text{ or } V = V_0 \cdot e^{\alpha T} \quad \dots \quad \dots \quad (iii)$$

A closer scrutiny brings out the significance of this  $V_0$  to be a hypothetical volume calculated on the assumption of the independence of  $\alpha$  on the temperature down to absolute zero ( $T=0$ ). Equation (ii) being quite general, if we consider the liquid state of the substance in question,  $V_0$  will stand for the imaginary volume of the liquid at absolute zero, calculated on the assumption that  $\alpha$  remains constant and is equal to that of the liquid.

In actual cases most liquids solidify at their freezing points long before the absolute zero is reached, and the volume which it is possible to get at absolute zero by extrapolation (because attainment of absolute zero is an impossibility from thermodynamic considerations) should refer more correctly to the volume of the solid state calculated on the basis of the constancy of the coefficient of expansion of the solid down to zero temperature. Of these two volumes [viz., the volume of the liquid extrapolated to absolute zero ( $V_{0l}$ ) and that of the solid state extrapolated down to the same temperature ( $V_{0s}$ ) on the assumption of the constancy of their respective coefficients of expansions] both of which are imaginary, the one of the solid state will be slightly larger than the other because  $\alpha$  for the solid is lower than that of the liquid. As a matter of approximation, these two extrapolated values may be regarded as equal to each other for all practical purposes. Thus for the hydrocarbon  $C_{20}H_{42}$ , whose specific volumes at different temperatures both in the solid and liquid states could be obtained from the literature, the ratio of these extrapolated values amounts to  $V_{0s} : V_{0l} = 1.016 : 1$ \*. Hence, passing

\* These data have been obtained from "The Physical and Thermodynamic Properties of Hydrocarbons" (*loc. cit.*).



from specific to molecular volume, we can approximately accept the molecular volume  $V_T$  of a liquid at any temperature

$$V_T = V_{01} \cdot e^{\alpha T} = V_{0s} \cdot e^{\alpha T} \quad \dots \quad \dots \quad (iv)$$

which signifies that the molecular volume of a liquid at any temperature,  $T$ , is equal to  $e^{\alpha T}$  times the volume of the same substance in the solid state at absolute zero. The equation (iv), although approximate, is a general one following directly from the definition of the coefficient of thermal expansion.

Now assuming that the fluidity of a liquid is a function of its free volume (cf. Batschinski, *loc. cit.*, Eyring and co-workers, *J. Phys. Chem.*, 1937, 41, 249) we may represent it mathematically as

$$\phi = F(V_f)$$

where  $F$  stands for any function and  $V_f$  for the free volume in the sense used by Eyring (*J. Chem. Phys.*, 1936, 4, 283) being the empty volume in a liquid within which the centre of a molecule can move and produce the viscous flow.

Expanding the function by McLaurin's theorem we get

$$\phi = a_0 V_f^0 + a_1 V_f^1 + a_2 V_f^2 + a_3 V_f^3 + \dots + a_n V_f^n + \dots$$

where  $a_0, a_1, a_2$  etc., are constants.

From calculations based upon the velocity of sound in the liquid state it has been possible to establish that

$$\phi = a_1 V_f \quad \dots \quad \dots \quad \dots \quad (v)^*$$

all the other coefficients and indices being redundant (cf. Kincaid and Eyring, *J. Chem. Phys.*, 1938, 6, 620).

If a liquid is cooled, its free volume gradually decreases till at a temperature  $T_s$ , where  $V_f$  becomes zero, the liquid loses its fluidity. Absence of free volume in a liquid does not necessarily signify that there is no empty space between liquid molecules. In fact, there may be some empty space still whose magnitude gradually diminishes as the temperature is cooled down, but the molecules cannot move within it and produce the viscous flow. The extrapolation of the volume of a liquid down to absolute zero is thus justified.

Now at  $T_s$ , where  $\phi$  just disappears we have from equation (iv)

$$V_{T_s} = V_{0s} \cdot e^{\alpha T_s} \quad \dots \quad \dots \quad \dots \quad (vi)$$

which indicates that the fluidity of a substance starts at that temperature ( $T_s$ ) where the volume of the substance becomes  $e^{\alpha T_s}$  times its volume at absolute zero.

This conclusion is interesting because it leads to a rough picture of how and where the fluidity of any substance starts. Again since  $V_{0s}$  stands for

\*This equation (v) will be established from experimental data in a future communication in connection with some other problem.

the molar volume of the solid at absolute zero, where the solid is expected to be in a perfect crystalline state with the highest possible close-packed structure, this may be regarded as the actual volume of all the molecules in a mole of the substance. Hence dividing  $V_{0s}$  by  $N$ , the Avogadro's number, we get approximately the actual volume of a single molecule. Similarly by dividing  $V_{T_s}$  by  $N$  we get the average volume of a molecule of the substance at temperature  $T_s$ , where its fluidity just starts. Since at  $T_s$  the close packing, which obtains at absolute zero, will be disturbed, this average volume per molecule at  $T_s$  includes the actual volume together with the empty space surrounding this. The ratio of these two, viz., the average volume of the molecule to the actual volume (as calculated from its molar volume at  $0^\circ$  absolute) will be equal to

$$V_{T_s}/V_{0s} = e^{\alpha T_s} \quad \text{by equation (vi)} = a, \text{ say} \quad \dots \quad (vii).$$

Thus  $e^{\alpha T_s}$ , which represents the intercepts in the figures (cf. equation i), signifies the ratio ( $a$ ) of these volumes, from which it is clear that the fluidity of a liquid will start at a temperature  $T_s$  where the average volume per molecule will be  $e^{\alpha T_s}$  times its actual volume. For the aliphatic hydrocarbon chain the volume of  $e^{\alpha T_s}$  has been observed to be 1.25 as shown in the table.

It may be mentioned here that the simple picture on the basis of which the foregoing relation is derived, although quite fascinating, is, however, far removed from the state of things prevailing in an actual process. The extrapolation of the fluidity lines as presented in the above figures to intersect the  $e^{\alpha T}$ -axis has been carried out under two simplifying assumptions :

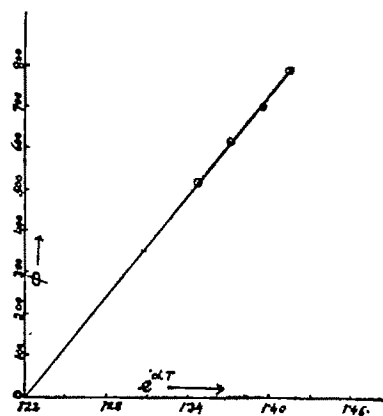
(i)  $\alpha$  remains constant over the entire temperature range considered, and (ii) no other factors appear to interfere with the fluidity at these temperatures down to  $T_s$ , excepting the disappearance of the free volume of the liquid. These assumptions, however, do not conform to reality because it is well known that, at low temperatures, as molecules approach closer and closer, not only Van der Waals' force of attraction and a diminished repulsive effect due to decreased thermal agitation but also other forces which are operative in the solid state gradually make their appearance and influence the phenomenon of transition from the liquid to the solid state. Hence, a difference between the temperature of fluidity ( $T_s$ ) and the actual freezing point ( $T_m$ ) of a liquid is but natural and up to the expectation. But still a study of this transition in the light of the 'hole theory' is interesting as will be appreciated from the considerations set forth below.

*Verification from Experimental Data*

It will now be examined how far the conclusions derived from equation (vi) conform to experimentally observed facts. From surface pressure measurements the cross-section of normal paraffin chains has been calculated to be 21 sq. Å (cf. Langmuir, *J. Amer. Chem. Soc.*, 1918, 40, 361). Since the area of the cross-section is independent of the length of the hydrocarbon chain, the 21 sq. Å has been regarded as an approximate value of the cross-section of the  $-\text{CH}_2$  group. X-ray observations on long chain hydrocarbons and their derivatives indicate that the area of the cross-section of this group in the crystal is about 18.5 sq. Å (vide Glasstone, "Recent Advances in Physical Chemistry", 1933, 2nd Ed., p. 332). These values of 21 sq. Å from surface films and 18.5 sq. Å for the crystalline solids may be regarded as the average cross-section of a  $\text{CH}_2$  group in the liquid state devoid of any free volume and its actual cross-section, the former being greater because it involves some empty space as well. The cross-sections are therefore in the ratio 21 : 18.5 whence, assuming the  $-\text{CH}_2$  group to be spherical, the volumes of the same group in the liquid and solid states will be related to each other (21 : 18.5) which equals 1.21. A  $-\text{CH}_2$  group should thus show an increase of volume to the extent of 1.21 times that of its actual volume and any compound made up essentially of  $-\text{CH}_2$  groups, like paraffin hydrocarbons, is expected to show an expansion to the same extent.

This point of view will be corroborated if, in the case of methane which is essentially composed of  $-\text{CH}_2$  groups, the intercept of  $(\phi - e^{\alpha T})$  line on the

FIG 3.  
Methane.



$e^{\alpha T}$  -axis agrees with this value of 1.21. The actual value amounts to 1.220 which is in excellent agreement with this value (vide Fig. 3).

Other normal hydrocarbons, however, all uniformly yield a value of 1.25 which indicates that molecules in these hydrocarbons need further separation for the appearance of fluidity. Methane is a spherically symmetrical molecule which the other members of the series are not, and it is easy to understand that in the case of spherical symmetry, the average intramolecular separation necessary for the appearance of fluidity should be less than those cases where spherical symmetry is absent. A slight difference between these values for methane (1.220 and 1.250) can thus be understood although all these hydrocarbons are essentially made up of  $-\text{CH}_2$  groups.

The values of  $a$  (vide equation *vii*) as presented in Table I may find explanation in the light of the same considerations. A slightly higher or lower value observed in some series, might be attributed to the relative importance of the  $-\text{CH}_2$  groups in the particular series as well as their position and orientation in determining the degree of assymetry. Thus, the lower members of the  $n$ -mercaptans exhibit greater deviation than the higher members where there is a perceptible tendency to come back to the value of 1.220 (the value of  $a$  for methane), due probably to the increase in the number of  $-\text{CH}_2$  groups in the compounds.

Benzene and its homologues present points of further interest. Benzene itself yields a value of  $a=1.162$ . From toluene, where at least one  $-\text{CH}_2$  group is present, this ratio jumps to 1.236 which is almost equal to that of methane, but slightly lower than that of the other paraffins. It is not unlikely that this latter owes its origin to the presence of the planar benzene ring itself in the molecule. In *cyclopentane* and *cyclohexane* series (cf. Table I) the values of  $a$  equal 1.252 and, although in these compounds there are five-membered and six-membered rings, higher values of  $a$  compared to the benzene homologues may be due to the difference in the nature of these rings from that of benzene. The coincidences of the values of  $a$ , as observed in this case, with those of the normal paraffins may likewise be looked upon as an effect of the presence of  $-\text{CH}_2$  groups in these, whereas in the benzene ring there is no  $-\text{CH}_2$  group. The importance of  $-\text{CH}_2$  group is further supported by the fact that the normal homologues of *cyclopentane* and *cyclohexane* yield  $a=1.252$  which compares favourably with  $a=1.250$  in the case of the olefine homologues. Although in the former two series there is a ring in the molecule and in the latter there is a double bond, the coincidence in the values of  $a$  for these series might be attributed to some common factor viz., the  $-\text{CH}_2$  groups in these compounds.

Thus, it is evident that the obvious conclusions which can be reached on this point from evidences cited above may be summarised by the statement that fluidity in any substance becomes possible when each of its molecules remains surrounded by sufficient empty space so that one can easily slide past another. In this picture a bigger molecule may not necessarily require larger space for its movement but an assymetric molecule would require larger space than a symmetrical one and a branched chain will necessarily require wider separation from each other before it can flow without being hindered by other molecules. The ratio  $a (=e^{\alpha T_s})$  which is a measure of the separation necessary for the appearance of fluidity will have a higher value as the assymetry in the molecule increases. Thus, in the case of the isomers of propylbenzene, the value of  $a$  for  $n$ -propylbenzene equals 1.236, which is equal to that for other normal homologues of benzene, while the *isopropylbenzene*,\* with a  $-\text{CH}_2$

group in the side, yields  $\alpha=1.248$ . Again for the two isomers : 1-methyl-4-ethylbenzene and 1:2:4-trimethylbenzene, the former is symmetrical and yields a value  $\alpha=1.232$ , while the latter which is lacking in symmetry shows  $\alpha=1.260$ . The values of  $\alpha$  in the case of *ortho*-, *meta*- or *para*-xylenes, all of which are symmetrical, yield  $\alpha=1.236$ , the same as that of other benzene homologues. All these facts lend further corroboration to the view points presented above.

The author's best thanks are due to Prof. S. N. Mukherjee, D. Sc., and to Prof. H. L. Roy, Dr. Ing., for their kind interest and valuable suggestions and to the authorities of the Institution for providing facilities to work in their library and laboratories.

PHYSICAL CHEMISTRY LABORATORY,  
COLLEGE OF ENGINEERING & TECHNOLOGY,  
JADAVPUR, CALCUTTA-32.

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## STUDIES ON RANCIDITY OF BUTTERFAT. PART VII. INFLUENCE OF WATER AND HUMIDITY ON RANCIDITY

BY S. MUKHERJEE

The effect of increased humidity is to enhance the rate of hydrolytic rancidity of the fat. It has been found that oxidative rancidity is retarded at very high humidities, viz., 90-100%.

It has been a common observation that oils and fats are hydrolysed in contact with moisture, and early investigators generally attributed to water the property of accelerating the development of rancidity in fats, and some even believed its presence essential for the process. It was, however, shown by later workers in the field that moisture, though increased enzymatic and microbial spoilage, under certain circumstances retarded rancidity as judged by odour and taste. Rancidity appears much more readily in dry samples of milk-powder than in those containing 2-3% of water (Holm, Wright and Greenbank, *J. Dairy Sci.*, 1927, 10, 33). It was also demonstrated that with mixtures of cod-liver oil and milk-powder, addition of 10% of water greatly delayed the development of "tallowy" flavour (Anderegg and Nelson, *Ind. Eng. Chem.*, 1926, 18, 620). With pure fats, it has also been observed (Greenbank and Holm, *ibid.*, 1924, 16, 598) that water increased the duration of the induction period of butterfat at 95° though most recent investigations failed to detect any influence on the induction period of lard at 50° (French, Olcott and Mattill, *ibid.*, 1935, 27, 724). Lea ("Rancidity in Edible Fats", Chem. Pub. Co., p. 184) reports that films of lard suspended over water have been found to oxidise less rapidly than similar films suspended over concentrated  $H_2SO_4$ .

It has been established by the author in a previous paper (Part IV, this *Journal*, 1950, 27, 557) that the influence of water consists essentially in causing an increased hydrolysis of the glycerides. In this paper the effect of storage of butterfat at 37° at different relative humidity has been studied. If the fat contains much water, the humidity of the atmosphere will be of less importance. Hence in the present study anhydrous butterfat has been used throughout.

### EXPERIMENTAL

The samples were kept stored in small pyrex glass beakers kept in desiccators over  $H_2SO_4$  of different concentrations so as to give the following relative humidities : 25%, 35%, 50%, 65%, 75%, 90% and finally 100% by storing over water in a desiccator. The acid concentrations were determined graphically from the table given by Willson (*Ind. Eng. Chem.*, 1921, 13, 329) correlating the strength of  $H_2SO_4$  and relative humidities at different temperatures.

The experimental results are shown in Table I, where progress of rancidity has been determined by acid and peroxide values.

TABLE I  
*The effect of atmospheric humidity on hydrolysis and oxidation of butterfat at 37°.*

Expt. No.	Relative humidity.	Acid and peroxide values after											
		15 days.		30 days.		45 days.		60 days.		90 days.			
		A.V.	P.V.	A.V.	P.V.	A.V.	P.V.	A.V.	P.V.	A.V.	P.V.		
1	25%	0.04	0.0	0.08	1.24	0.36	1.58	0.43	6.98	1.03	10.3		
2	35	0.06	0.0	0.03	1.17	0.40	1.70	0.52	6.14	1.21	8.0		
3	50	0.06	0.0	0.09	0.63	0.43	1.28	0.73	3.3	1.47	9.7		
4	65	0.06	0.0	0.09	1.06	0.43	1.70	0.74	7.7	1.68	12.4		
5	75	0.06	0.0	0.09	1.06	0.43	1.30	0.74	3.34	1.70	7.2		
6	90	0.09	0.0	0.10	0.74	0.47	1.00	0.94	1.46	1.90	5.7		
7	100	0.13	0.0	0.18	0.44	0.76	0.78	1.10	0.86	2.25	2.0		
8	Control (dry)	0.0	0.05	0.05	0.20	0.24	1.0	0.34	2.3	0.50	9.0		
9	Control (moisture)	0.2	0.14	0.43	0.30	0.70	2.4	1.3	3.0	2.0	18.0		

The results of these experiments are shown graphically in Figs. 1 and 2.

FIG. 1  
*Effect of atmospheric humidity on hydrolysis.*

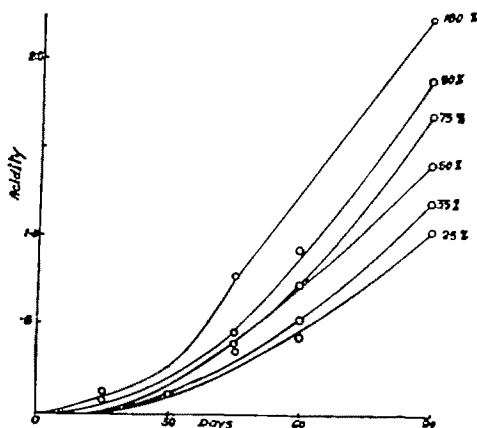
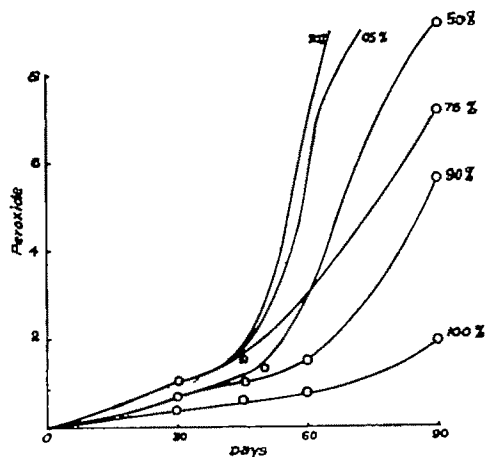


FIG. 2  
*Oxidation at 37° at diff. relative humidities.*



It is evident that anhydrous fat samples, when kept in humid atmosphere, undergo hydrolytic rancidity, the degree of which increases with increase in atmospheric humidity; the effect is maximum at 90-100% humidity. Oxidation is also seen to proceed at a rate faster than the control sample in the samples 1-4. The rate of development of oxidative rancidity, as indicated by peroxide formation, is, however, slower at very high humidities (Expts. 6 and 7) than the control sample. This may tentatively be explained as follows.

The amount of moisture available at the surface of a fat sample depends on the water content of the latter and on the humidity and rate of movement of air. If the water content of the fat is nill, humidity will play the prominent role in the development of hydrolytic rancidity. In such cases it may be assumed that rancidity will develop by diffusion of moisture and oxygen from the surface to the interior of the fat, the rate of which will depend on their respective concentrations. In this case probably both oxygen and moisture are competing for the surface of the fat, and it is highly probable that at very high humidities the rate of diffusion of moisture into the fat is greater than that of oxygen, with the ultimate result that the rate of oxidation is slower at higher relative humidity (cf. experiments 6 and 7). The most reasonable conclusion to be drawn from the data is that water probably has a slightly retarding effect on the rate of absorption of oxygen by pure fats.



## ANALYTICAL CHEMISTRY OF THORIUM. PART IV. SEPARATION FROM URANIUM

BY T. K. S. MURTHY, B. R. LAKSHMANA RAO AND  
BH. S. V. RAGHAVA RAO

Separation of thorium from uranium by the classical oxalic acid method is not satisfactory in that the ignited oxide is slightly coloured. *m*-Nitrobenzoic acid and *o*-chlorobenzoic acid are shown to give highly satisfactory results in the presence of 50 to 60 times of uranium in a second precipitation.

Dutt (this *Journal*, 1945, 22, 75) from a critical study of the various methods for the separation of thorium from uranium, concluded that the oxalic acid method gave accurate results in U/Th ratio up to 200. Ryan, McDonell and Beamish (*Ind. Eng. Chem. Anal. Ed.*, 1947, 19, 410) employed Ferron with success up to U/Th ratio of 2; when, however, larger amounts of uranium were present, a double precipitation was necessary and the thorium recovery was only 90%. Our experiments indicated that although from the consideration of  $\text{ThO}_2$  weighed the oxalic acid method was unsatisfactory, the oxide residue left on ignition was coloured pale yellow even at small U/Th ratio and a pure *white* residue could be obtained only on a second precipitation. On account of the difficulty in dissolving the oxalate, a second precipitation presents a particular disadvantage. In this investigation *m*-nitrobenzoic acid and *o*-chlorobenzoic acid have been employed with the same success, and with the advantage that the precipitate is easily soluble in mineral acids. Although satisfactory results were obtained in a single precipitation, the residue showed always a slight yellow tinge, which certainly pointed to contamination by uranium. The amount of uranium, thus carried, however, was very small, a fraction of a milligram, and tests for thorium in the filtrate were negative. Thus, for most purposes of assay of uranium minerals for thorium, a single precipitation will be sufficient.

### EXPERIMENTAL

*Preparation of the Reagents.*—Pure thorium nitrate solution was prepared in the manner already reported (vide Part I in this series, this *Journal*, 1950, 27, 457). The thorium content of this solution was estimated with oxalic acid and *m*-nitrobenzoic acid (10 ml. of the solution gave 0.0567 g. and 0.0568 g. of  $\text{ThO}_2$  respectively).

A sample of pure uranium oxide (Merck) was dissolved in nitric acid and crystallised twice from distilled water. The crystals on desiccation were weighed and dissolved in water. The  $\text{U}_3\text{O}_8$  content was checked by

precipitation with redistilled ( $\text{CO}_2$  free) ammonia and ignition; 10 ml. of the solution gave 0.1116 g. of  $\text{U}_3\text{O}_8$  as against 0.1117 g. theoretical. Measured volumes of the two solutions were mixed for obtaining different U/Th ratios.

Preliminary investigation indicated that uranium was co-precipitated by both the reagents at a  $p_{\text{H}}$  above 3.5, and below 2.6 the precipitation of thorium was incomplete. All the following separations were carried out in the  $p_{\text{H}}$  range of 2.6 to 2.8, a condition which was easily established by thymol blue imparting a slightly red tinge

*Procedure.*—The  $p_{\text{H}}$  was adjusted to the proper value by making the solution just orange to thymol blue. The thorium was then precipitated from hot, nearly boiling solution and washed with a dilute solution of the reagent. For a second precipitation the precipitate was dissolved in hot dilute nitric acid,

TABLE I

*Separation with m-nitrobenzoic acid.*

Expt. No.	$\text{ThO}_2$ taken.	$\text{U}_3\text{O}_8$ added.	$\text{ThO}_2$ found.	Difference.	Remarks.
A. Single precipitation.					
1	0.0568 g.	0.1116 g.	0.0574 g.	-0.0006 g.	Residue colored
2	0.0568	0.1116	0.0572	+0.0004	slightly yellow
3	0.0568	0.2232	0.0579	+0.0011	in all cases.
B. Double precipitation.					
1	0.0568 g.	0.2232 g.	0.0568 g.	0	
2	0.0568	0.5580	0.0569	+0.0001	
3	0.0568	1.1160	0.0572	+0.0004	
4	0.0568	3.3120	0.0572	+0.0004	Residue white.
5	0.0142	0.1658	0.0142	0	
6	0.0284	0.1658	0.0283	-0.0001	
7	0.0284	0.3356	0.0283	-0.0001	

*o-Chlorobenzoic Acid.*—The procedure is similar to precipitation with *m*-nitrobenzoic acid.

TABLE II

*Separation with o-chlorobenzoic acid.*

Expt. No.	$\text{ThO}_2$ taken.	$\text{U}_3\text{O}_8$ added.	$\text{ThO}_2$ found.	Difference.	Remarks
Single precipitation.					
1	0.0583 g.	0.1116 g.	0.0581 g.	-0.0002 g.	Residue colored
2	0.0568	0.2232	0.0573	+0.0005	yellow.
3	0.0568	0.2232	0.0569	+0.0001	

Expt. No.     $\text{ThO}_2$  taken.     $\text{U}^3\text{O}^8$  added.     $\text{ThO}_2$  found.    Difference.

B. Double precipitation.

4	0.0568	0.2232	0.0568	0
5	0.0568	0.5580	0.0568	0
6	0.0568	0.9926	0.0568	0
7	0.0568	0.4815	0.0567	-0.0001
8	0.0284	0.1240	0.0283	-0.0001
9	0.0284	0.2480	0.0285	+0.0001
10	0.0142	0.1240	0.0141	-0.0001
11	0.0142	0.2480	0.0142	0

It is thus evident that uranium in concentration up to 60 times that of thorium can conveniently be removed in a double precipitation by either *m*-nitrobenzoic acid or *o*-chlorobenzoic acid in the  $p_{\text{H}}$  range of 2.6 to 2.8.

CHEMICAL LABORATORIES,  
ANDHRA UNIVERSITY,  
W A L T A I R.

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STUDIES ON RANCIDITY OF BUTTERFAT. PART VIII. CHEMICAL  
ACCELERATORS OF RANCIDITY. THE EFFECT OF PEROXIDES  
AND VOLATILE PRODUCTS OF OXIDATION OF FAT  
ON RANCIDITY

By S. MUKHERJEE

Addition of a very small amount of rancid fat greatly reduces the induction period of fresh fats, whilst products of oxidation of fats have no effect on the development of rancidity of fresh fat.

The interaction of oxygen with fats and oils provides curves typical for auto-catalytic reaction, characterised by a phase of slow change which precedes rapid oxidation; this period of slow oxidation has been described as the 'induction period' of the fat. This induction period is of greatest practical importance since it determines the length of time for which a product can be kept in storage without becoming rancid. The explanation usually advanced to account for this induction period is that some product or products of the reaction, most probably the peroxides, function as positive catalyst in promoting further oxidative changes, these substances being considered to accumulate in the fat until present in sufficient concentration to produce intense oxidation. Besides peroxides, it has also been questioned whether the volatile products of oxidation can act as accelerators in the development of rancidity by autoxidation. Greenbank and Holm (*Ind. Eng. Chem.*, 1924, 16, 598) found that when air was led through butterfat in three bottles in succession, rancidity developed first in bottle No. 3 and last in bottle No. 1. This was ascribed to the accelerating effect of the volatile products of oxidation. The more recent work by Roschen and Newton (*Oil & Soap*, 1937, 14, 17) does not agree with their observation.

In this paper the effect of addition of small quantities of an oxidised sample of butterfat to a fresh fat, as also the effect of passing the volatile products of an oxidised sample through a fresh sample have been studied. In experiments 1 and 2 (Table I) respectively 1 and 5% of a rancid butterfat, whose peroxide value was 50, were added to a freshly prepared fat which showed no peroxide value.

To study the effect of volatile products of oxidation on the development of rancidity, a slow stream of nitrogen from a cylinder, absolutely freed from oxygen by passage through alkaline pyrogallol, was passed for 8 hours through a sample of highly rancid fat (P.V. 50), kept over a boiling water-bath, and the evolved gases, necessarily carrying the volatile products of oxidation (giving strongly aldehydic reaction), were then passed through a series of three conical flasks containing fresh butterfat

kept in a molten state in a bath at 40°. After the experiments, the contents of the different flasks were mixed together and stored at 37°, keeping the necessary control. Another experiment was performed to study the effect of the residual fat (rancid) obtained after the volatile aldehydes were removed by the nitrogen stream. The results are shown in Table I.

TABLE I

*Effect of addition of peroxides and volatile products of oxidation on the development of rancidity of butterfat.*

Description.	15 days		Kreis and peroxide value after				60 days	
			30 days		45 days			
	V. P.	K. V.	P. V.	K. V.	P. V.	K. V.	P. V.	K. V.
1. Butterfat +1% rancid fat (P. V. 50.0)	0.8	2.0	4.9	4.8	16.5	9.8	33.0	13.2
2. Butterfat +5% rancid fat (P. V. 50.0)	0.95	2.0	5.0	4.5	18.4	10.0	42.1	12.6
3. Butterfat + volatile products of oxidation	0.15	1.1	1.3	1.6	2.3	4.2	3.5	6.5
4. Butterfat %1 residue of oxidised fat from expt. (3)	0.85	2.1	5.0	5.0	15.8	10.0	35.5	13.0
5. Control	0.15	0.1	1.1	1.5	2.4	4.5	3.3	8.0

From experiments No. 1, 2 and 4, it can be confirmed that such products of oxidation as peroxides can reduce the induction period considerably, nearly to half its original value. Hence, it may be concluded that the active constituents of oxidised fat, viz. the reactive peroxides, are responsible for a large proportion of the pro-oxidant effect of the oxidised fats and for the apparently autocatalytic nature of the process of autoxidation and rancidity. On the other hand, the stability of the fresh fats towards oxidation is found to be practically unaffected by the volatile oxidation products, as evident from the peroxide and Kreis figure in Table I (cf. No. 3). Hence it may be concluded that the materials volatile at the boiling point of water which include the products responsible for rancid odour, are inactive as catalysts for the oxidation of butterfat.

Another group of strong chemical accelerators of oxidation are the metals. In view of their profound importance both from theoretical as also from industrial point of view they are dealt in a separate communication.

## REACTION OF SUGARS WITH GELATIN

BY R. D. ADVANI AND C. S. NARWANI

Addition of 0.5–3.0 m. mols. of aldo- and keto-sugars per 100 c. c. of 1% gelatin–water-sol gives a definite decrease in  $p_H$  values varying with the nature of the sugars in the following order: mannose > glucose = *l*-arabinose = xylose > galactose > fructose > maltose > lactose.

From the study of the electrometric titration curves of the various mixtures of gelatin sol and sugars against standard NaOH solution, it is concluded that the condensation power of each sugar varies with the  $p_H$  of the mixture.

Kostychev and Brillant (*Z. physiol. Chem.*, 1923, 127, 224) found a reaction between glucose and amino-acids at 55° in slightly alkaline solutions leading to a diminution of detectable amino group, thus showing a combination of  $-NH_2$  group of amino-acid and  $-CHO$  group of glucose. Gullard and Mead (*Biochem. J.*, 1935, 29, 397) titrated electrometrically with hydrogen electrode, gelatin sol, in presence of aromatic aldehydes, with NaOH and judged the chemical combination between them quantitatively by the extent of deflection from the pure gelatin curve. In the light of all these results a reaction of  $-CHO$  and  $=CO$  groups with  $-NH_2$  group of amino-acids of aqueous sol is presumed. Further, Frankel and Katchalsky (*ibid.*, 1937, 31, 1595) showed fructose to be inert, whereas Neuberg and Kobel (*Biochem. Z.*, 1925–1928) showed its combination with amino-acids resulting in a controversy.

With a view to ascertaining whether gelatin sol behaves like amino-acids towards sugars (a) measurements of the changes in acidity electrometrically with hydrogen electrode and (b) potentiometric titrations of mixtures of gelatin and various quantities of different aldo- and keto-monosaccharides (xylose, *l*-arabinose, glucose, mannose, galactose, fructose) and -disaccharides (maltose and lactose) with standard NaOH solution were made.

## EXPERIMENTAL

Throughout the investigation Jena glass apparatus and conductivity water, free from  $CO_2$ , were used. Merk's gold-label gelatin from the same packet, extra pure sugars and electrometrically prepared calomel were used. The gelatin sol was prepared as suggested by Shephard and Houck (*J. Phys. Chem.*, 1930, 34, 273). The hydrogen electrode vessel was of Bunker type (1920); it consisted of 1 cm. length of platinised Pt wire.

Hydrogen gas, prepared electrolytically and purified with  $KMnO_4$  and NaOH and hot copper filings was used for the  $H_2$ -electrode. Calomel electrode and hydrogen electrode were both placed in a water thermostat at 37° and connected through an agar-KCl bridge. The E.M.F. set up, was measured

with a slide wire potentiometer, using a sensitive ballistic mirror galvanometer. The authors found the following precautions with regard to hydrogen electrode greatly helpful:

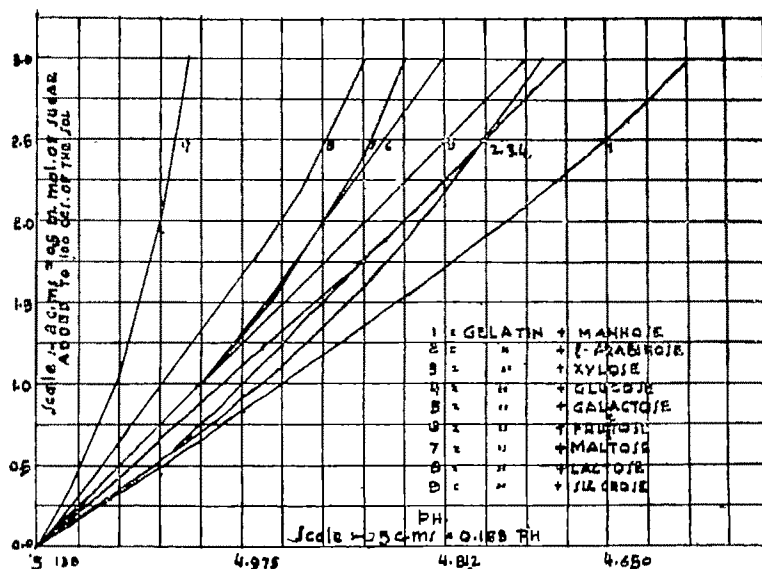
(1) Platinum wire of same length and thickness, platinised for exactly the same time, preserved under  $\text{CO}_2$ -free water, was used.

(2) For every experiment newly platinised electrode was used, and occasionally a new electrode was inserted in the middle of the experiment to see that the E. M. F. recorded was the same, and every experiment was repeated till fairly constant results were obtained.

(3) Hydrogen was passed over the electrode for five minutes, before it was allowed to come in contact with the solution.

The influence of addition of various quantities (0.5-3.0 m.mols. per 100 c. c.) of different sugars on the  $p_H$  of 1% gelatin sol is shown in Fig. 1.

FIG. 1



The electrometric titration curves of 20 c. c. of 1% gelatin sol containing 0.5 m.mol. of various sugars per 100 c. c. against 0.04N-NaOH are shown in Fig. 2; the quantities of 0.04N-NaOH required to reach the neutral point ( $p_H$  7) in case of various sugars are found to be nearly the same.

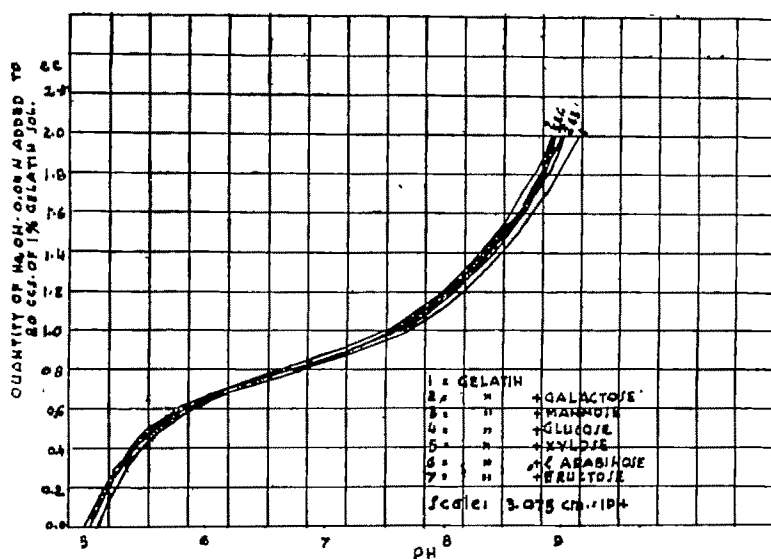
## DISCUSSION

Additions of aldo- and keto-monosaccharides to gelatin sol result in a definite decrease of  $p_H$  of the sol, and with an increase in the concentration of sugar, the  $p_H$  goes on decreasing as shown in Fig. 1, indicating condensation

of sugar with  $\text{NH}_2$  group. Pentoses, xylose and *L*-arabinose, follow practically the same course showing that the condensation power of pentoses with gelatin is nearly the same; the hexo-aldoses condense to different extents, following the order: mannose > glucose > galactose. Condensation power of fructose is less than that of aldoses. Combining both pentoses and hexoses we get the order: mannose > glucose = *L*-arabinose = xylose > galactose > fructose > maltose > lactose.

Potentiometric titration curves for the mixtures of gelatin and monosaccharoses (Fig. 2) are nearly similar to those obtained by Gulland and Mead

FIG. 2



(*loc. cit.*) in case of the mixtures of gelatin with formaldehyde or aromatic aldehydes, where maximum convergence takes place at 6.5  $p_H$ . The reaction as judged from the shifts in titration plots (not shown here) of various concentrations (0.5-3.0 m. mols) of each sugar from pure gelatin curve, is maximum in the case of first few concentrations and then goes on decreasing; the maximum convergence in case of xylose, *L*-arabinose, mannose, glucose and galactose takes place at 6.69, 6.76, 6.53, 6.78 and 6.7  $p_H$  values respectively; plots of fructose are slightly different from those of aldoses, maximum convergence in this case taking place at 6.0  $p_H$ ; the reaction with first 0.5 m. mol. % is much more than any other concentrations.

Addition of aldo-disaccharides of gelatin sol decreases the  $p_H$  value of the sol as shown in Fig. 1, though to a much lesser extent than monosaccharides. In the case of non-reducing sugar, saccharose, there is a slight decrease in  $p_H$ , perhaps due to decrease in free solvent owing to hydration of sugars, but much less



than that of aldo-sugars, showing that there is practically no condensation of this sugar with  $\text{NH}_2$  group of gelatin.

Alkaline potentiometric titration curves (not shown here) for mixtures of gelatin and aldo-disaccharides resemble those in the case of monosaccharides though the shifts in the case of the former are much less than those of the latter. The reaction as judged from the shifts in titration plots (not shown here) of various concentrations (0.5-3.0 m. mols %) from pure gelatin curve, is maximum in the case of first few concentrations and then goes on decreasing ; the maximum convergence in the case of lactose and maltose occurs at 6.2 and 6.59  $p_H$  values respectively.

Generalising the results, it is concluded that aldo- and keto-sugars condense with  $\text{NH}_2$  group of gelatin sol, resulting in an increase in the acidity of the sol, though the condensation power of each sugar varies to a different extent, and that the shifts in the titration curves are true measures of the reaction, since Urban and Shaffers (*J. Biol. Chem.*, 1932, **94**, 697) have shown that negligible quantity of alkali is required for neutralisation of sugars. From the increase in the divergence of the titration curves with alkalinity or acidity of the medium, it is concluded that the condensation power of the sugars increases with alkalinity and acidity.

CHEMICAL LABORATORY,  
S. B. GARDA COLLEGE,  
NAVSARI.

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## PHYSICO-CHEMICAL STUDIES ON THE STABILITY OF ETHYLENE DIBIGUANIDE COMPLEX OF TRIPOSITIVE SILVER

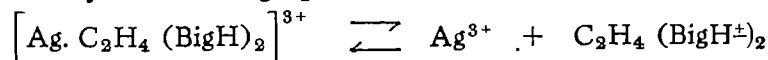
BY DEBABRATA SEN, NRIPENDRA NATH GHOSH AND PRIYADARANJAN RÂY

The stability of ethylenedibiguanide complex of tripositive silver in aqueous solution has been determined from the equilibrium constant of the reaction between the complex and the hydrogen ion, and the acid dissociation constants of the base ethylenedibiguanide. The equilibrium constant was derived from a knowledge of the  $p_H$  value of the acid solution containing the complex and of the concentration of  $Ag^{3+}$  ion therein. The latter was derived from the measurement of redox potential of the acid solution of the complex salt in presence of  $Ag^+$  ion and ethylenedibiguanide. The value obtained for the instability constant was found to be of the order of  $10^{-32}$ , representing a very high degree of stability for the complex, as against  $10^{-34}$  for the cobaltamines, and approaches that of cobaltic *tris*-biguanide complex ( $10^{-35}$ ) determined by De, Ghosh and Rây (previous communication).

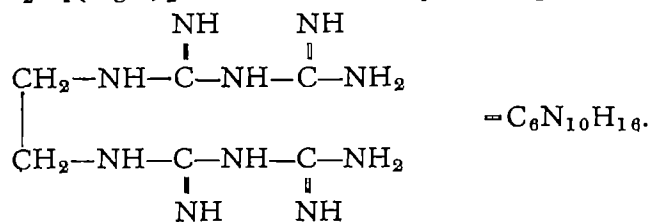
The occurrence of tripositive silver has been proved by Luther and Pokorny (*Z. anorg. Chem.*, 1908, 57, 290), as also by Carman (*Trans. Faraday Soc.*, 1934, 30, 566). This has been supported fully by the preparation of many complex compounds of tripositive silver in pure state by Malaprade (*Bull. soc. chim.*, 1935, v, 2, 359; 1936, 3, 361; 1938, 5, 582; *Compt. rend.*, 1937, 204, 979), Malatesta (*Gazzetta*, 1941, 71, 467, 480) and by Rây and Chakravarty (this *Journal*, 1944, 21, 47).

The present work deals with the determination of the stability of a well established tripositive silver complex of ethylenedibiguanide, prepared in this laboratory (Rây and Chakravarty, *loc. cit.*). The substance forms an inner metallic complex of the third order (Rây and Dutt, this *Journal*, 1948, 25, 563) with quite a high degree of stability; its nitrate in nitric acid solution (dil.) can be heated almost to boiling without any appreciable decomposition. The ethylenedibiguanide behaves as a quadridentate ligand and the tripositive silver shows a co-ordination number of four. Each silver atom is bound by two primary and two secondary valencies to the ethylenedibiguanide molecule, which latter binds again two hydrogen ions. The substance therefore presents many interesting features of study.

The dissociation of the silver ethylenedibiguanide complex may be represented by the following equation:



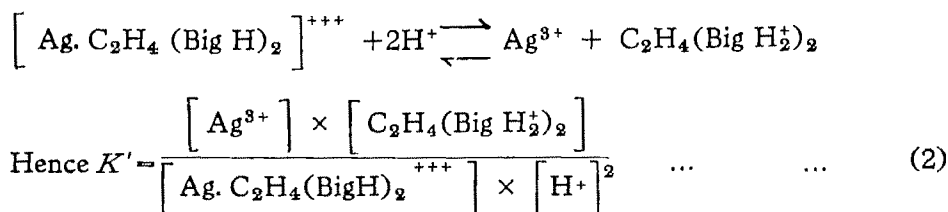
where  $C_2H_4 (BigH)_2$  = a molecule of ethylenedibiguanide =



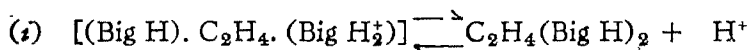
Therefore,

$$K = \text{the instability constant} = \frac{[Ag^{3+}] \times [C_2H_4(BigH^+)_2]}{[Ag.C_2H_4(BigH)_2^{+++}]} \quad \dots \quad (1)$$

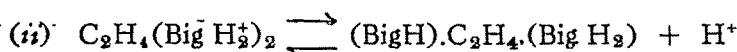
In order to obtain  $K$ , the equilibrium constant  $K'$  of the decomposition reaction, given below, has to be first determined :



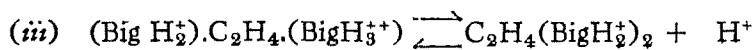
Ethylenedibiguanide can at most behave as a tetra-acidic base, and its acid dissociation constants  $k_1^*$ ,  $k_2^*$ ,  $k_3^*$ , and  $k_4^*$  are given by :



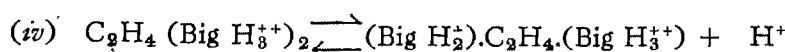
$$\text{Therefore, } k_1^* = \frac{[C_2H_4(BigH)_2] \times [H^+]}{[(BigH).C_2H_4.(BigH_2^+)]} \quad \dots \quad (3)$$



$$\text{Therefore, } k_2^* = \frac{[(BigH).C_2H_4.(BigH_2)] \times [H^+]}{[C_2H_4(BigH_2^+)_2]} \quad \dots \quad (3a)$$



$$\text{Therefore } k_3^* = \frac{[C_2H_4(BigH_2^+)] \times [H^+]}{[(BigH_2^+).C_2H_4.(BigH_3^{++})]} \quad \dots \quad (4)$$



$$\text{Therefore, } k_4^* = \frac{[(BigH_2^+).C_2H_4.(BigH_3^{++})] \times [H^+]}{[C_2H_4(BigH_3^{++})_2]} \quad \dots \quad (4a)$$

Now from (3) and (3a),

$$[C_2H_4(BigH_2^+)_2] = \frac{[C_2H_4(BigH)_2] \times [H^+]^2}{k_1^* k_2^*},$$

combining this with (2) we get, the instability constant  $K = K' \cdot k_1^* \cdot k_2^*$ .

The equilibrium constant,  $K'$ , can be determined by knowing  $[Ag^{3+}]$ ,  $[H^+]$ ,  $[C_2H_4(BigH_2^+)_2]$  and  $[Ag.C_2H_4(BigH)_2^{+++}]$ . Of these,  $[H]$  ion can be obtained by measuring the  $p_H$  of the solution and  $[C_2H_4(BigH_2^+)_2]$  from the following relation.

Let  $x$  be the total biguanide added, then

$$x = [C_2H_4(BigH_3^{++})_2] + [(BigH_2^+).C_2H_4.(BigH_3^{++})] + [C_2H_4(BigH_2^+)_2]$$

{neglecting  $[(\text{BigH}) \cdot \text{C}_2\text{H}_4 \cdot (\text{BigH}_2^+)]$  and  $[\text{C}_2\text{H}_4(\text{BigH})_2]$ , as the measurements were made in acid solutions}.

Therefore, from (4) and (4a),

$$x = [\text{C}_2\text{H}_4 (\text{BigH}_2^+)_2] \left( 1 + \frac{[\text{H}^+]}{k_3^*} + \frac{[\text{H}^+]^2}{k_3^* \cdot k_4^*} \right)$$

$$\text{Hence, } [\text{C}_2\text{H}_4 (\text{BigH}_2^+)_2] = \frac{x \cdot k_3^* \cdot k_4^*}{k_3^* \cdot k_4^* + k_4^* \cdot [\text{H}^+] + [\text{H}^+]^2} \quad \dots \quad (5)$$

Now, in order to find out  $[\text{Ag}^{3+}]$ , the oxidation potential of the complex silver ethylenedibiguanide nitrate in presence of  $\text{Ag}^+$  ion and ethylenedibiguanide ion in acid and water solution was determined against a saturated calomel electrode. From this, provided that the normal redox potential of that argentic (III)—argentous (I) system is known, the concentration of the  $\text{Ag}^{3+}$  ion in a solution of the complex salt can be calculated from the well known equation :

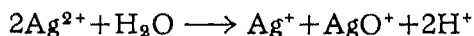
$$E = E_0 + \frac{RT}{nF} \ln \frac{a_{\text{Ag}^{3+}}}{a_{\text{Ag}^+}} \quad \dots \quad (6)$$

where  $E$  is the observed E.M.F., corrected to normal hydrogen electrode ;  $E_0$ , standard electrode potential for argentic (III)—argentous (I) system, and  $n=2$  ;  $a_{\text{Ag}^{3+}}$  and  $a_{\text{Ag}^+}$  are the activities of  $\text{Ag}^{3+}$  and  $\text{Ag}^+$  ions in solution, which become practically equal to their respective concentrations in dilute solutions. The value of  $E_0$ , however, is not definitely known, nor is its determination easy. It was, however, approximated from the E.M.F. of the following cell, measured by Luther and Pokorny (*Z. anorg. Chem.*, 1908, 57, 290) at 25°.

$\text{Pt} | \text{Ag}_2\text{O}_3, \text{Ag}_2\text{SO}_4 \text{ saturated} | - | 0.5N\text{-H}_2\text{SO}_4, \text{H}_2 | \dots + 1.74 \text{ volt.}$

If it be permitted to assume that the normal electrode potential of argentic (III)—argentous (I) system does not vary to any great extent from the above value of 1.74 volts, then the value of  $\text{Ag}^{3+}$ -concentration can be computed from the equation. As the temperature coefficient of electrode potentials is generally of the order of  $10^{-3}$  to  $10^{-4}$ , the value of  $E_0$  at the temperature of the experiment has been recalculated with the temperature coefficient value of +0.0017 in analogy with that of the  $\text{Co}^{3+}-\text{Co}^{2+}$  system (Lamb and Larson, *J. Amer. Chem. Soc.*, 1920, 42, 2024).

It should, however, be pointed out here that Noyes and Kossakoff (*ibid.*, 1935, 57, 1238) obtained a normal oxidation potential of 1.914 volts for the system consisting of unipositive and bipoisitive silver ions in nitric acid solution. Noyes and co-workers have further shown that the bipoisitive silver ion in aqueous solution changes more or less rapidly by dismutation into tripositive and unipositive silver ions :



This seems to suggest that tripositive silver is more stable than its bipoisitive state. We may therefore with some justification adopt the value, +1.74 volts, as the redox potential for  $\text{Ag}^{3+}-\text{Ag}^+$  system, and that will give us a maximum limit for the instability constant  $K$  of the complex. •

## E X P E R I M E N T A L

*Preparation of the Solutions*

*Ethylenedibiguanide Nitrate.*—Ethylenedibiguanide acid sulphate was prepared and purified by recrystallisation from hot water containing a little sulphuric acid (Rây and Chakravarty, this *Journal*, 1944, 21, 41). (Found :  $\text{SO}_4$ , 42.64.  $\text{C}_6\text{H}_{16}\text{N}_{10}$ ,  $2\text{H}_2\text{SO}_4$ ,  $1.5\text{H}_2\text{O}$  requires  $\text{SO}_4$ , 42.57 per cent).

The sulphate (2.2602 g.) was taken in a 500 c.c. volumetric flask. A little water was added to this and then 20 c.c. of a 0.5*N*-KOH solution were added from a burette. Most of the substance went into solution leaving a small residue. The flask was then heated on the water-bath till a clear solution was obtained. A calculated quantity of *M*/5- $\text{Ba}(\text{NO}_3)_2$  solution (50 c.c.) was next added to it from a burette. The precipitated  $\text{BaSO}_4$  was allowed to settle overnight. The volume was made up to 501 c.c. (allowing 1 c.c. for the volume of the precipitate). The solution, which was free from  $\text{Ba}^{++}$  and  $\text{SO}_4^{--}$  ions, was then filtered. The strength of the nitrate ( $\text{C}_6\text{H}_{16}\text{N}_{10}$ ,  $2\text{HNO}_3$ ) solution, thus prepared, was *M*/100.

*Silver Nitrate Solution.*—A *M*/50-solution was prepared from a double-recrystallised sample of silver nitrate (Analar quality) ; 0.6794 g. of the substance was dissolved in water and the volume made up to 200 c.c.

*Potassium Nitrate Solution.*—A 2*M* solution was prepared by dissolving 40.44 g. of potassium nitrate (Kahlbaum reagent) in 200 c.c. of conductivity water.

*Nitric Acid.*—Chemically pure nitric acid was distilled in an all-glass apparatus. The first fraction contained some brown nitrous fumes and was rejected. The clear acid then distilling over was collected in a dry amber coloured bottle. The distillation was stopped before the whole of the acid distilled over. From this acid a 1.5*N* solution was prepared by checking with titration against sodium carbonate. From this latter, other solutions of weaker strength were prepared by necessary dilution.

*Silver Ethylenedibiguanide Nitrate.*—The complex nitrate was prepared and purified by recrystallisation from hot 2*N*- $\text{HNO}_3$ , following the procedure described by Rây and Chakravarty (*loc. cit.*). {Found : Ag, 20.62, 20.69 ;  $\text{Ag}^{3+}$ , 20.69.  $[\text{Ag}.\text{C}_2\text{H}_4(\text{BigH})_2](\text{NO}_3)_3$  requires Ag, 20.69 ;  $\text{Ag}^{3+}$ , 20.69 per cent}.

In all the determinations a Beckmann  $p_{\text{H}}$ -meter (model G) was used for the measurement of E. M. F. and  $p_{\text{H}}$  values.

*Determination of the Oxidation Potential*

A standard calomel electrode supplied with the apparatus was used as the reference electrode. This was not, however, directly dipped into the solution under examination, but was connected to the latter by a bridge liquid of  $\text{KNO}_3$  (2*M*) solution in order to reduce the liquid junction potential. The arrangement of the bridge was as follows: The calomel electrode was dipped into 2*M*- $\text{KNO}_3$  solution in a vessel, which had a capillary tube fused at its bottom that served to connect the liquid under examination with the calomel electrode. The platinum electrode in the case of potential measurement and glass electrode in the case of  $p_{\text{H}}$  measurement were dipped directly into the solution under examination. All the measurements were made after waiting for 10 to 15 minutes for equilibrium to be attained at the room temperature. Solution of the complex salt for each measurement was freshly prepared from the solid crystals.

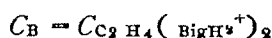
The results of the experiments are arranged in the following tables. *E* (corrected) refers to the E. M. F. corrected to standard hydrogen electrode. The values of  $k^*_1$ ,  $k^*_2$ ,  $k^*_3$ , and  $k^*_4$ , or their  $p_k$  values were taken from the work of B. Sarma (unpublished). These were determined by the measurement of  $p_{\text{H}}$  values of a solution of ethylenedibiguanide when progressively titrated with an acid.

TABLE I

$C_{\text{Ag}^+} = 0.0008M$ . Total ethylenedibiguanide = 0.0008*M*.  $t = 31^\circ$ .

$E_0 = 1.751$  volt.  $p k_1^* = 11.76$ ;  $p k_2^* = 11.34$ ;  $p k_3^* = 2.88$ ;  $p k_4^* = 1.74$

Complex.	$p_{\text{H}}$ .	$E$ (corr.).	$C_{\text{B}} \times 10^3$ .	$C_{\text{Ag}^{3+}}$ .	$p_{\text{K}}$ .	$p_{\text{Kc}}$ .
0.0032 <i>M</i>	3.47	0.9669	63.39	$7.13 \times 10^{-30}$	46.01	52.95
0.0016	3.67	0.9479	68.69	$1.67 \times 10^{-30}$	45.90	53.24
0.0008	3.87	0.9279	72.47	$35.74 \times 10^{-32}$	45.85	53.62
0.0004	4.00	0.9099	74.29	$9.18 \times 10^{-32}$	45.87	53.87
0.0002	4.08	0.8939	75.25	$2.71 \times 10^{-32}$	45.93	54.09
0.0001	4.30	0.8799	77.23	$9.18 \times 10^{-33}$	45.65	54.25



$$p_{\text{Kc}} (\text{mean}) = 53.67$$

TABLE II

 $C_{Ag^+} = 0.0008M$ , Total ethylenedibiguanide =  $0.0008M$ .  $t = 32^\circ$ .

 $C_{complex} = 0.0003M$ .  $E_0 = 1.752$  volt.  $pK_1^* = 11.76$ ;  $pK_2^* = 11.34$ ;

 $pK_3^* = 2.88$ ;  $pK_4^* = 1.74$ .

Acid.	pH.	$E$ (corr.).	$C_B \times 10^5$ .	$C_{Ag^{3+}}$ .	pK.	pKc.
0.200M	0.82	1.045	0.075	$0.032 \times 10^{-28}$	50.99	52.63
0.100	1.11	1.038	0.257	$0.019 \times 10^{-28}$	50.10	52.32
0.050	1.40	1.030	0.822	$0.101 \times 10^{-28}$	49.28	52.08
0.020	1.78	1.014	3.192	$0.291 \times 10^{-27}$	48.48	52.04
0.010	2.01	1.006	6.445	$1.596 \times 10^{-27}$	47.97	52.00
0.005	2.29	0.990	13.360	$4.710 \times 10^{-27}$	47.62	52.20
0.002	2.71	0.967	30.320	$8.375 \times 10^{-26}$	47.18	52.38
						$pKc$ (mean) = 52.26

TABLE III

 $C_{Ag^+} = 0.0008M$   $C_{complex} = 0.0008M$ .  $C_{HNO_3} = 0.025M$ .  $t = 35^\circ$ .

 $E_0 = 1.757$  volt.  $pK_1^* = 11.76$ ;  $pK_2^* = 11.34$ ,  $pK_3^* = 2.88$ ;  $pK_4^* = 1.74$ .

Et-dibiguanide.	pH.	$E$ (corr.).	$C_B \times 10^5$ .	$C_{Ag^{3+}}$ .	pK.	pKc.
0.0060 M	1.76	0.988	20.910	$0.475 \times 10^{-28}$	48.49	52.01
0.0032	1.76	0.994	11.950	$0.753 \times 10^{-28}$	48.53	52.05
0.0016	1.74	0.999	5.594	$1.104 \times 10^{-28}$	48.73	52.21
0.0008	1.73	1.006	2.705	$1.888 \times 10^{-28}$	48.84	52.30
0.0004	1.71	1.010	1.248	$2.559 \times 10^{-28}$	49.08	52.50
0.0002	1.70	1.013	0.613	$3.157 \times 10^{-28}$	49.32	52.72
						$pKc$ (mean) = 52.30

TABLE IV

 $C_{Ag^+} = 0.0008M$ . Total ethylenedibiguanide =  $0.0008M$ .  $t = 32^\circ$ .  $C_{HNO_3} = 0.05M$ 
 $E_0 = 1.752$  volt.  $pK_1^* = 11.76$ ;  $pK_2^* = 11.34$ ;  $pK_3^* = 2.88$ ;  $pK_4^* = 1.74$ .

Complex.	pH.	$E$ (corr.).	$C_B \times 10^5$ .	$C_{Ag^{3+}}$ .	pK.	pKc.
0.0032M	1.38	1.040	0.7614	$21.23 \times 10^{-28}$	49.64	52.40
0.0016	1.38	1.035	0.7614	$14.55 \times 10^{-28}$	49.50	52.26
0.0008	1.39	1.029	0.7914	$9.18 \times 10^{-28}$	49.36	52.14
0.0004	1.39	1.022	0.7914	$5.41 \times 10^{-28}$	49.29	52.07
0.0002	1.40	1.013	0.8230	$2.71 \times 10^{-28}$	49.25	52.05
0.0001	1.40	1.004	0.8230	$1.37 \times 10^{-28}$	49.25	52.05
						$pKc$ (mean) = 52.16

## DISCUSSION

From an examination of the tables, particularly Table II, it will be observed that the  $p_K$  values decrease with the rise of the  $p_H$  values of the solution containing the complex. This seems to suggest that stability of the complex increases with the acid concentration of the solution. This is apparently supported by the general behaviour of a solution of the silver ethylenedibiguanide nitrate which can be boiled in 2*N*-HNO<sub>3</sub> solution without any noticeable change. In fact, the substance is purified, as already described, by recrystallisation from dilute nitric acid solution. But a distinction should be made between the decomposition and dissociation of the complex. It is the decomposition of the complex which is actually retarded by the hydrogen ion, whereas dissociation constant should have remained constant under all conditions, if all our assumptions were correct. The tripositive silver ion is, however, more or less unstable and in aqueous solution breaks down possibly as follows:



So, in the determination of the redox potential for  $\text{Ag}^{3+}$ — $\text{Ag}^+$  system, the above reaction should preferably be taken into consideration in place of the simple  $\text{Ag}^{3+} + 2e \rightleftharpoons \text{Ag}^+$ , as assumed for the calculation of  $C_{\text{Ag}^{3+}}$  and  $p_K$  values of the tables.

A recalculation of  $C_{\text{Ag}^{3+}}$  and  $p_K$  values on this basis gives more or less a constant  $p_K$  value in each table for the temperature of measurement. These are denoted by the symbol  $p_{Kc}$ , i.e.  $p_K$  corrected. The  $p_{Kc}$  values can, however, be readily obtained from  $p_K$  values by the use of the expression

$$p_{Kc} = p_K + 2p_H.$$

For,  $\ln \frac{C_{\text{Ag}^{3+}}}{C_{\text{Ag}^+}}$  in the equation for E.M.F. is to be substituted by

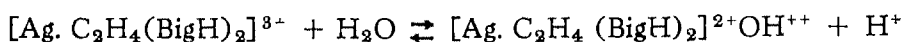
$$\ln \frac{C_{\text{Ag}^{3+}}}{C_{\text{Ag}^+} \times [\text{H}^+]^2}.$$

Hence the value of  $C_{\text{Ag}^{3+}}$  in our equation (1) for the instability constant,  $K$ , will be  $[\text{H}^+]^2$  times the value employed before.

These  $p_{Kc}$  values have been added as a separate column in each table at the end. This brings to a closer agreement among values in all other tables excepting those in Table I, ignoring, however, the slight differences of temperature. The individual  $p_{Kc}$  values in Table I also differ somewhat largely among themselves. This may be attributed to two causes: (a) hydrolysis of the complex salt in solutions of low acidity giving rise to basic cations; (b) increased tendency of the tripositive silver ion,  $\text{Ag}^{3+}$ , to break up into  $\text{Ag}^+$ ,  $\text{H}^+$  and oxygen gas rendering the redox reaction at



the electrode rather more or less irreversible. Hydrolysis of the complex salt occurs as follows :



Further hydrolysis may lead to a still basic ion,  $[\text{Ag. C}_2\text{H}_4(\text{LigH})_2]\text{OH}^{++}(\text{OH})_2$ . So, the concentration of the pure complex ion is thereby altered. In solutions of moderately low  $p_{\text{H}}$  values this salt hydrolysis of the complex is more or less completely retarded. The  $p_{\text{Kc}}$  value for the silver ethylene-dibiguanide complex may thus be regarded as approximately equal to 52, representing, so to say, its maximum range of instability. The extraordinary stability of this inner complex of tripositive silver is hereby established, in keeping with its general behaviour. The value of its instability constant approaches closely that of the *tris*-biguanide cobaltic complex ( $10^{-36}$  approx.) described previously by De, Ghosh and Ray (this *Journal* 1950, 27, 493), and is considerably smaller than that of the cobaltammines investigated by Lamb and Larson (*loc. cit.*), which are of the order of  $10^{-34}$ .

INORGANIC CHEMISTRY LABORATORY,  
UNIVERSITY COLLEGE OF SCIENCE,  
CALCUTTA.

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## SPONTANEOUS CRYSTALLISATION FROM SUPERSATURATED META-STABLE SOLUTIONS

BY B. S. SRIKANTAN

The supersolubility range  $T_s - T_c$  for inorganic salts follows closely the nature of the solubility curves. For substances whose temperature coefficient of solubility is constant throughout the range from 0° to 100°, the value of  $T_s - T_c$  is constant at different temperatures. A change in the temperature coefficient of solubility denotes also a change in the value of the limit of supersaturation. Substances like  $\text{KClO}_4$ ,  $\text{NH}_4\text{Cl}$  and  $\text{PbAc}_2$ , which have meta-stable regions in their normal solubility range, display tendency to stabilisation against spontaneous crystallisation, if heated beyond the meta-stable region and cooled. Saturated solutions of hydrates, which have transition temperatures and dissolve in their water of crystallisation on heating, maintain high supersolubility and stabilise against spontaneous crystallisation on heating and cooling, possibly due to high solubility of the less hydrated species at low temperatures.

Miers and Issac (*J. Chem. Soc.*, 1906, 89, 413) demonstrated that if aqueous solutions of salts were cooled and *kept continuously shaken*, at a particular temperature, a copious shower of minute crystals appeared throughout the solution. This phenomenon occurred at quite different temperatures for each solution according to their strength. This temperature is identified as that at which spontaneous crystallisation begins in supersaturated solutions. The author (this *Journal*, 1949, 26, 60) has shown that the condition for spontaneous crystallisation on supercooling in the meta-stable region is dependent on the particle size of the solute in equilibrium with the saturated solution and has drawn conclusion that the substances like copper sulphate, sodium thiosulphate will exhibit high supersolubility on cooling, but those like sodium chloride and barium chloride will show greater tendency for spontaneous crystallisation than maintaining supersolubility. The minimum size of particle for spontaneous crystallisation has been shown to be  $50\mu$ . But in most supersaturated solutions experimented upon, the adjustment of uniform sizing of particles, from which the supersaturated solutions are to be made, is a matter of considerable practical difficulty. In practice therefore, saturated solutions made at any temperature, if cooled without crystallisation, are considered supersaturated at the lower temperatures and  $T_s - T_c$  (where  $T_s$  is the temperature of saturation and  $T_c$ , the temperature where crystallisation begins) as the regions at which supersaturation exists in the meta-stable state. It is the object of this investigation to study the behaviour of different substances in this region at different temperatures.

### EXPERIMENTAL

The chemicals used in this investigation were highly pure, being either of Merck or Khalbaum. The water for preparing solutions was distilled five times over in Pyrex vessels and stored in Jena glass bottles.

TABLE I

$T_s$ .	$T_s - T_c$ .	Average $T_s - T_c$ .	
1. Potassium chloride.			
40	12.6 (54) ; 12.8 (65)	12.7	
50	13.3 (65)	13.3	
60	13.0 (62) ; 13.4 (62) ; 13.2 (72)	13.2	
70	13.0 (72) ; 13.6 (90)	13.3	13.1
2. Potassium nitrate.			
A			
10	3.8 (15)	3.8	
20	3.8 (25) ; 3.4 (25)	3.6	
30	4.4 (31) ; 4.6 (31)	4.5	3.9
B			
40	7.8 (42)	7.8	
50	7.8 (52) ; 7.8 (52) ; 7.8 (55)	7.8	
60	7.2 (62) ; 7.9 (62)	7.6	
70	8.0 (71) ; 8.0 (72) ; 8.0 (72)	8.0	7.8
3. Boric acid.			
A			
10	6.0 (17) ; 6.1 (25)	6.1	
20	6.0 (28) ; 6.4 (28)	6.2	
30	6.8 (36)	6.8	6.4
B			
40	7.6 (45) ; 7.8 (55)	7.7	7.7
C			
50	10.0 (65) ; 10.0 (75) ; 10.2 (85)	10.1	
60	10.2 (65) ; 10.6 (75) ; 10.6 (85) ; 10.4 (95) ; 10.4 (95)	10.5	10.3
D			
70	12.2 (72) ; 12.5 (85) ; 13.0 (95)	12.8	12.8
4. Potassium perchlorate.			
A			
10	6.2 (15)	6.2	6.2
B			
20	2.6 (45) ; 2.6 (60)	2.6	
40	2.6 (45)	2.6	
50	2.6 (52) ; 2.4 (65) ; 2.4 (75) ; 2.1 (85)	2.4	
60	2.2 (65) ; 2.0 (65)	2.1	2.4
C			
70	No supersaturation ; within 0.1° below the temperatures there is a shower of crystals.		
80			

TABLE I (*contd.*)

$T_s$ .	$T_s - T_c$ .	Average $T_s - T_c$ .	
5. Ammonium chloride.			
A			
10	3.4 (12) ; 3.4 (30) ; 3.8 (50)	3.5	
20	3.8 (22) ; 3.8 (52) ; 4.0 (35)	3.8	
30	3.6 (33) ; 4.0 (60)	3.5	
40	3.4 (43) ; 3.6 (43) ; 3.6 (43)	3.8	3.7
A <sub>1</sub>			
	7.6 (55) ; 7.9 (65)	7.8	7.8
B			
50	5.2 (54)	5.2	
60	5.2 (62) ; 5.4 (62)	5.3	5.3
B <sub>1</sub>			
50	9.0 (65) ; 10 (77)	9.5	9.5
C			
70	6.0 (72) ; 6.8 (71) ; 6.4 (71)	6.4	6.4
(N. B. In the last case the shower of crystals was meagre)			
6. Sodium thiosulphate.			
10	No crystallisation till 0° (11) ; 25 (70).		
7. Potash alum.			
10	5 (15) ; 5 (15) ; Nil (30, till—5°.)		
20	17 (24) ; Nil (40) till—6°C.		
30	26.2 (35) ; 28.0 (30) ; Nil till—7 (61)		
40	38.0 (42) ; 37.6 (43) ; Nil till—7 (61)		
50	40.0 (52) ; Nil till—7 (70)		
60	38.0 (63) ; 38.5 (63) ; Nil till—8 (70)		
8. Lead acetate.			
A			
10	8.4 (42)	8.4	
20	8.0 (24) ; 8.0 (24) ; 8.2 (40)	8.1	8.3
A <sub>1</sub>			
	26.6 (60)		
B			
30	15.5 (31) ; 14.5 (32)	15.0	
B <sub>1</sub>			
	21.0 (50) ; 20.0 (60)		
40	15.0 (42) ; 15.0 (42)	15.0	
	23.5 (62)		15.0
C			
50	33.0 (52) ; 33.0 (51) ; 33.5 (51)	33.2	33.2

The figures in parenthesis indicate the highest temperatures to which the solutions were heated above  $T_s$  in each case.

The apparatus used was a small bulb, like that of the specific gravity bottle, about 7.5 c.c. in capacity with a well ground-in stopper. The above distilled water (5 c.c.) was taken in the bulb. The substance to be examined was weighed out carefully, according to its solubility, in 5 c.c. at the temperature of the experiment. The solubility data from the International Critical Tables were taken. The bulb was stoppered and hung in a large beaker of water by a thin wire. By means of the wire the bottle could be kept continuously shaken during the experiment. The beaker was slowly heated by means of a micro-burner and kept at the required temperature by adjustment of the flame. Temperatures below the room temperature were obtained by circulating water from melting ice. Experiments were conducted at different temperatures of saturation  $T_s$ , and temperatures were raised above this a number of times and allowed to fall slowly, all the while the solution in the bulb was kept shaking. At  $T_c$  there was a shower of crystals throughout the solution as described by Miers and Issac (*loc. cit.*).

This observation of the shower of crystals could be repeated any number of times with the same solution, alternately heating and cooling or with a fresh solution. The temperature was measured by means of a thermometer reading up to  $0.1^\circ$ . The data under each set of conditions were thoroughly repeatable in that the shower of crystals came down in each case at temperatures differing by less than  $0.5^\circ$ . Before cooling, the solutions were heated to higher temperatures than  $T_s$  and were kept there for 5 to 30 minutes and allowed to cool. Table I describes the results.

## DISCUSSION

The results are best discussed in relation with the solubility curves of the substances and the temperature coefficient of solubility of them at different temperatures. From the solubility curves (not shown here) three types of curves are possible ideally: (i) where the temperature coefficient of solubility is constant throughout the range, (ii) where it changes continuously, and (iii) those of the hydrates which exhibit transition temperatures between the anhydrous and the hydrated forms of the substances. Majority are mixed types of (i) and (ii). Table II gives the temperature coefficients of the molal solubility (per 1000 g. of water) of the substances under review at different temperatures. This table has been computed with the aid of the molal solubilities from the International Critical Tables. The temperature coefficient of solubility at any temperature  $T$  is calculated as:

$$\frac{S_{T+5} - S_{T-5}}{10}$$

where  $S_{T+5}$  and  $S_{T-5}$  are the molal solubilities at  $5^\circ$  above and below the temperature  $T$ , respectively.

TABLE II

	Temperature coefficient of solubility at temperatures of Substance,								
	10°.	20°.	30°.	40°.	50°.	60°.	70°.	80°.	90°.
KCl	0.04	0.04	0.04 ✓	0.04	0.04	0.04	0.04	0.04	0.04
KNO <sub>3</sub>	0.09	0.12	0.15	0.20	0.23	0.27	0.29	0.33	0.35
H <sub>3</sub> BO <sub>3</sub>	0.02	0.03	0.03	0.04	0.06	0.06	0.07	0.10	0.14
KClO <sub>4</sub>	0.003	0.005	0.007	0.009	0.015	0.022	←— M. S. —→		
NH <sub>4</sub> Cl	0.07	0.08	0.08	(M. S.)	0.085	(M. S.)	0.09	0.10	0.11
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 5H <sub>2</sub> O	0.06	0.07	0.10	0.26	0.28	0.19	0.12	—	—
	←— 5 aq —→		←— 48.2 —→		←— 2 aq —→		←— 70 —→		←— S —→
K <sub>2</sub> SO <sub>4</sub> , Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , 2H <sub>2</sub> O	0.006	0.008	0.011	0.018	0.03	0.03	0.07	—	—
PbAC <sub>2</sub> , 3H <sub>2</sub> O	0.04	0.06	0.11	0.23	←— M. S. —→				

M. S. denotes meta-stable and S, anhydrous substance.

The solubility curve for KCl is straight and the temperature coefficient of solubility is constant throughout the range. The supersolubility limit,  $T_s - T_c$ , is constant and the heating of the solution to higher temperatures than  $T_s$  and cooling do not affect the temperature of spontaneous crystallisation. To this class of substances belong others like NaCl, KBr, KI and K<sub>2</sub>SO<sub>4</sub>.

The case of potassium nitrate is different. The solubility coefficient with temperature increases rapidly from 10° to 30°. Between 40° and 70° it is less rapid, and again changes to a different value. Corresponding to this behaviour,  $T_s - T_c$  shows different values (A) between 10° and 30° and (B) between 40° and 70°. Similar is the behaviour of boric acid; it shows four sets of such values up to 70°. Heating to higher temperatures does not affect the value of  $T_s - T_c$ . The temperature coefficient of solubility of KClO<sub>4</sub> gradually increases from 0.003 at 10° to 0.22 at 60° and thereafter with higher temperatures no more extra solubility is known, but even the saturated solution is meta-stable. Table I shows that the values for the supersaturation limit from 20° onward is constant till 60°. Heating to higher temperatures does not affect the value. At 70° and 80° no supersaturation is maintained and  $T_s - T_c$  is hardly 0.1°.

The temperature coefficient of solubility of NH<sub>4</sub>Cl is constant between 10° and 30°. At 40° and 60° the saturated solution is itself meta-stable. After 60° the values for temperature coefficient are slightly different from those of the previous ones but constant among themselves. At 50°, where there is no metastability, the value is between those at 40° and 60°.

The value of  $T_s - T_c$  is 3.7 between 10° and 30° and is constant.

Heating to a higher temperature does not affect the value so long as the  $T_s$  is within  $30^\circ$ . But the saturated solution at  $40^\circ$ , if heated beyond the intermediate stable temperature, *i. e.*  $50^\circ$ , there is stabilisation and the value of  $T_s - T_c$  is 7.8 ( $A_1$  in Table I). Again, the value of  $T_s - T_c$  is different at  $50^\circ$  and  $60^\circ$ , but constant; if the saturated solutions at these temperatures are not heated much beyond  $60^\circ$ , the second meta-stable state of the saturated solution, they do not show any tendency to stabilisation. Data  $B_1$  at  $50^\circ$  show that stabilisation against spontaneous crystallisation could be obtained by heating above the second meta-stable region of solubility. In the normal region at and above  $70^\circ$ , the value of  $T_s - T_c$  is again low and constant.

It is clear from the above that the region of supersaturation,  $T_s - T_c$ , depends on the nature of the solubility of the substance at different temperatures; and if the solubility curve exhibits a meta-stable region, heating the saturated solution above this and cooling, stabilise the solution against spontaneous crystallisation or the value of  $T_s - T_c$  is increased *e. g.*,  $A_1$ ,  $B_1$  for  $NH_4Cl$  and  $PbAc_2$ .

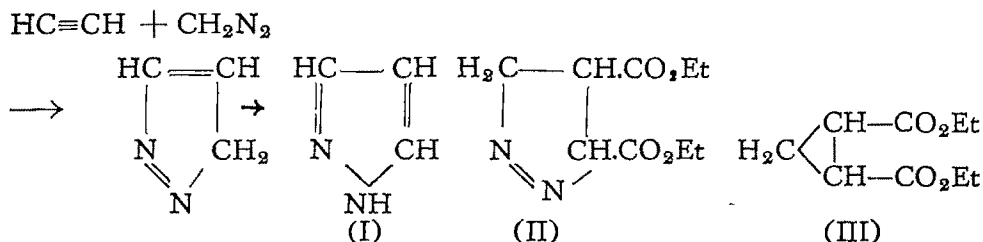
Substances like sodium thiosulphate, alum and lead acetate show again a different behaviour. These possess sufficient water of crystallisation in which their corresponding anhydrides are soluble. They all exhibit transition temperatures. On heating the saturated solutions of these substances the transformation to the less hydrated or anhydrous state may possibly proceed to some extent even before the transition temperature, where complete transformation takes place. The solution on heating therefore contains the hydrated and also the dehydrated species. There is a greater amount of anhydrous molecules than hydrated ones as one approaches the transition temperature. The anhydrous substances show a decrease in solubility with increase of temperature, which means that the anhydrous species dissolve more on cooling. Hence, considerable cooling has to be done before spontaneous crystallisation takes place. They therefore maintain high range of supersolubility.  $ZnSO_4$ , acetic acid,  $CdSO_4$  and  $Na_2SO_4$  are a few examples of this class of substances.

## THE STABILITY OF *cyclo*PROPANE RING THROUGH ADDITION REACTION OF DIAZOMETHANE

By S. G. GHATE, R. KAUSHAL AND S. S. DESHAPANDE

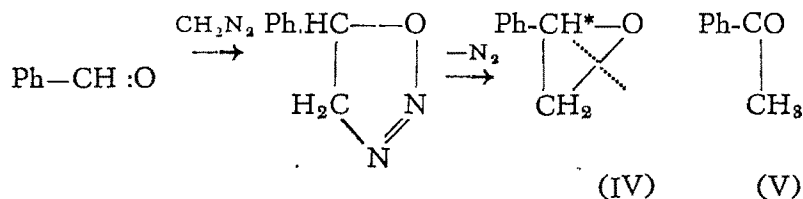
Diazomethane reacts additively with benzalacetophenone and benzalacetone to give pyrazoline derivatives. These loose nitrogens, on heating pass into *cyclo*propane derivatives which are unstable and by opening up the ring and migration of hydrogen they isomerise to ethylenic compounds. Thus, there is the possibility of synthesising substances which should theoretically result by condensation of two different ketones but which are not so obtained in practice.

In the Buchner-Curtius reaction diazomethane or its substitution product reacts additively with a molecule containing a double or a triple bond. Thus, Pechmann (*Ber.*, 1898, 31, 2950) by condensing diazomethane with acetylene obtained pyrazole (I).



Similarly from fumaric ester and diazomethane Buchner (*Annalen*, 1893, 273, 226) obtained pyrazole-4 : 5-dicarboxylic ester (II). The pyrazoline compounds are generally stable and, when solid, could be crystallised without decomposition. When, however, they are heated, nitrogen is evolved and the pyrazoline ring gives rise to *cyclo*propane ring. For instance, by heating the compound (II) Buchner (*ibid.*, 1893, 273, 216) obtained *cyclo*propane-1:2-dicarboxylic ester (III) and Guha (*Ber.*, 1937, 70, 1890) synthesised *trans*-caronic ester (III, Me<sub>2</sub> in place of H<sub>2</sub>) by condensing dimethyldiazomethane with fumaric ester.

Schlotterbeck (*Ber.*, 1907, 40, 479) treated diazomethane with benzaldehyde containing a double bond between carbon and oxygen when acetophenone (V) was obtained according to the following reaction :



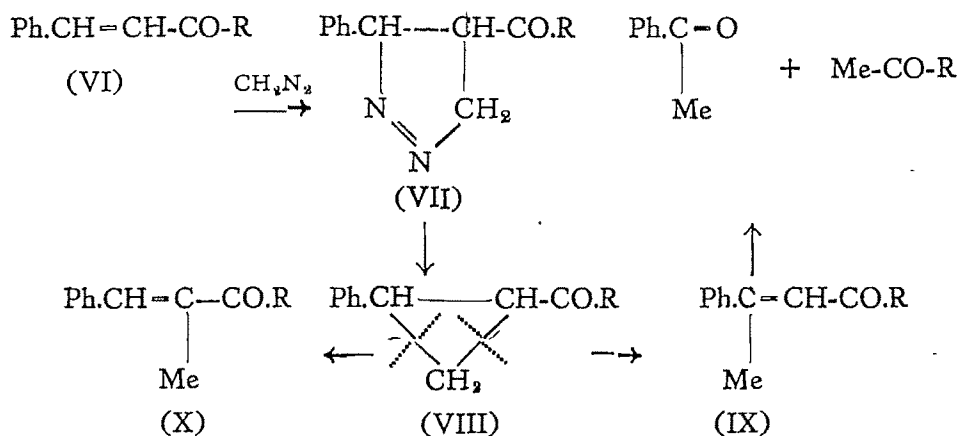
\*Generally when condensations are attempted between two different compounds of the same class, one or the other of them undergoes self-condensation and the desired product to be formed from two different molecules is not formed (unpublished observation).



If the above is the correct course of the reactions, it is clear that the ethylene oxide ring (IV) is less stable than *cyclopropane* ring. It therefore opens up between  $\text{CH}_2$  and O, and the hydrogen marked with an asterisk migrates to  $\text{CH}_2$  and turns it into  $-\text{CH}_3$ , while oxygen is linked up to carbon by a double bond forming acetophenone (V). This change is facilitated by the presence of a negative group in the aldehyde molecule.

The question now arises whether such a transformation is possible in a *cyclopropane* ring also as it is in ethylene oxide ring, provided that (a) one of the three carbons is present as  $\text{CH}_2$  to become  $\text{CH}_3$  after migration of hydrogen and (b) a negative group is present in the molecule directly linked to carbon of *cyclopropane* ring.

Benzalacetophenone (VI,  $\text{R} = \text{Ph}$ ) was therefore condensed with diazomethane when the pyrazoline compound (VII,  $\text{R} = \text{Ph}$ ) was formed. On elimination of nitrogen it was expected to give *cyclopropane* derivative (VIII,  $\text{R} = \text{Ph}$ ), which satisfied both the conditions (a) and (b) mentioned above. If the *cyclopropane* ring (VIII) becomes unstable as the ethylene oxide ring (IV), and if it opens up at one or the other dotted line, it should give after migration of hydrogen the structure (IX or X,  $\text{R} = \text{Ph}$ ).



Compounds (VIII), (IX) and (X) are isomeric. The compound (IX,  $\text{R} = \text{Ph}$ ) should be identical with the product obtained by self-condensation of acetophenone.

Generally, when the pyrazoline compound is heated under reduced pressure, nitrogen is eliminated and *cyclopropane* ring is closed. But the compound (VII,  $\text{R} = \text{Ph}$ ) sublimed over unchanged. It was therefore heated in a sulphuric acid bath at  $210^\circ\text{--}220^\circ$  at ordinary pressure till evolution of nitrogen ceased and the resulting viscous liquid distilled at  $165^\circ\text{--}166^\circ/2\text{mm.}$ , analysis of which corresponds to the composition required for phenylbenzoyl*cyclopropane* (VII,  $\text{R} = \text{Ph}$ ).

Its properties, however, are not what one should expect for *cyclopropane* compound (VIII). Thus it immediately decolorises bromine in  $\text{CCl}_4$

and  $\text{KMnO}_4$  in water. Above all, when heated with strong hydrochloric acid it gives a quantitative yield of acetophenone; even if a few drops are heated in a test tube, the smell of acetophenone is perceptible. These properties are explained by the structure (IX,  $\text{R}=\text{Ph}$ ) which has a double bond and which on hydrolysis gives two molecules of acetophenone. On referring to the literature (cf. Kohler, (*Amer. Chem. J.*, 1904, 31, 658) the compound (IX,  $\text{R}=\text{Ph}$ ) proved to be diphone obtained by the condensation of acetophenone with itself and was confirmed by comparing the oximes of the substance and of diphone. It seems therefore that the pyrazoline compound (VII) first gives rise to *cyclo*propane compound (VIII) as usual, and that in the latter conditions, (a) and (b) mentioned above, being satisfied, the *cyclo*propane ring undergoes the same change as the ethylene oxide ring (IV).

If the above views are correct, diazomethane should afford a method of synthesising substances which should theoretically result by the condensation of two different ketones, but which in practice cannot be obtained in this way\*. For instance, though (IX,  $\text{R}=\text{Me}$ ) is expected to be formed by condensing acetone with acetophenone, the condensation does not materialise in practice and the compound does not appear to have been prepared so far.

Benzalacetone (VI,  $\text{R}=\text{Me}$ ) therefore was treated with diazomethane when the pyrazoline compound (VII,  $\text{R}=\text{Me}$ ) was obtained. This was found to be very stable and on distillation under reduced pressure with or without copper powder it sublimed unchanged. It was then heated at  $200^\circ$  for 4 hours when evolution of nitrogen was complete and the resulting liquid distilled at  $108^\circ\text{--}109^\circ/3$  mm. Analysis corresponds to  $\text{C}_{11}\text{H}_{12}\text{O}$  required for the isomeric structures (VIII, IX, and X,  $\text{R}=\text{Me}$ ).

Like (IX,  $\text{R}=\text{Ph}$ ), the liquid decolorises aqueous potassium permanganate, bromine in  $\text{CCl}_4$  and forms a semicarbazone (m.p.  $180^\circ$ ). From this behaviour and analogy with the compound obtained from benzalacetophenone (VI,  $\text{R}=\text{Ph}$ ) it follows that the *cyclo*propane ring has not survived during heating of the pyrazoline derivative (VII,  $\text{R}=\text{Me}$ ) and has been transformed into the structure (IX,  $\text{R}=\text{Me}$ ). It cannot obviously be the isomeric  $\gamma$ -benzylidene-ethylmethyl ketone (X,  $\text{R}=\text{Me}$ ) which has been described by Harries and Mullar (*Ber.*, 1902, 35, 968) as a crystalline solid (m.p.  $38^\circ$ ). Further, like (IX,  $\text{R}=\text{Ph}$ ) it undergoes hydrolysis on boiling with hydrochloric acid and gives acetophenone.

## EXPERIMENTAL

Diazomethane was prepared by a modification of the method described by Werner (*J. Chem. Soc.*, 1919, 115, 1093). The preparation and all reactions were carried out in a fume chamber.

*3-Phenyl-4-benzylpyrazoline* (VII,  $\text{R}=\text{Ph}$ ).—To 10 g. of benzalacetophenone (m.p.  $56^\circ$ ) (Kohler and Chadwell, "Organic Synthesis", 1922, vol. 2, p. 1), dissolved in

dry ether (75 ml.) was added gradually a well cooled solution of diazomethane from 10 g. of nitrosomethylurea (Brochet and Gambier, *Bull. soc. chim.*, 1895, *iii*, 13, 533; Bell, *Chem. News*, 1875, 32, 99). When the addition was complete, the flask was fitted with a reflux condenser provided with a calcium chloride tube and left in a thermos at 0°. Next day very fine crystals appeared, which did not increase further even after 4 days. The crystals were removed and after drying weighed 8 g. The ethereal liquid after decomposing the excess of diazomethane with acetic acid gave no more of the product. It was crystallised from alcohol as fine yellowish needles, m.p. 132°. (Found: C, 76.3; H, 5.4; N, 12.0.  $C_{16}H_{14}ON_2$  requires C, 76.8; H, 5.6; N, 11.2 per cent).

It does not react with semicarbazide hydrochloride or nitrophenylhydrazine.

*Removal of Nitrogen by the Action of Heat on the Pyrazoline Compound (VII, R=Ph) and Formation of (IX, R=Ph).*—The compound (VII, R=Ph, 6.0 g.) was heated in a test tube with a long air condenser in a sulphuric acid bath, the temperature being gradually raised to 210° and maintained at 210°-220° for 3 hours until the evolution of nitrogen had ceased. The brown viscous oil left distilled at 164°-166°/3 mm., yield 4 g. (Found: C, 87.1; H, 6.0.  $C_{16}H_{14}O$  requires C, 86.5; H, 6.3 per cent).

It is a pale yellow, pleasant smelling liquid, which is sparingly soluble in alcohol. It does not react with semicarbazide or phenylhydrazine but decolorises bromine in  $CCl_4$  and aqueous  $KMnO_4$ . On heating alone it gives the smell of acetophenone.

*Hydrolysis of (IX, R=Ph).*—The liquid (1 ml.) was refluxed with 50% hydrobromic acid (15 ml.) on a sand-bath and then steam-distilled. The distillate on extraction with ether and removal of the solvent gave a small quantity of a liquid, which was characterised as acetophenone by the smell and formation of the semicarbazone, m.p. 198°. When, however, hydrobromic acid was replaced by hydrochloric acid, the hydrolysis was better effected and the yield of acetophenone was almost theoretical. Thus 2 g. of (IX, R=Ph) gave 1.5 g. of acetophenone.

The *oxime* of (IX, R=Ph) was prepared by refluxing for 5 hours 0.5 g. of the substance with 0.25 g. of hydroxylamine hydrochloride in absolute alcohol and pouring in a large excess of water when the oxime separated as a white precipitate. It was crystallised from alcohol as white monoclinic crystals, m. p. 132°, which proved to be the oxime of diphenone.

*3-Phenyl-4-acetylpyrazoline (VII, R=Me).*—Benzalacetone (10 g.) in dry ether (75 ml.) was treated with ethereal diazomethane (150 ml.) from 15 g. of nitrosomethylurea at 0°. On the third day the crystals separating were removed and weighed (8 g.). From the ethereal solution after decomposing

the excess of diazomethane and removing the solvent, a second crop was obtained; the total yield was 11 g. It was crystallised from alcohol in fine light yellow needles, m. p.  $96^{\circ}$ . It is sparingly soluble in water and ether and soluble in benzene and gives no characteristic colour with ferric chloride solution. (Found: C, 70.4; H, 6.5; N, 14.3.  $C_{11}H_{12}ON_2$  requires 70.0; H, 6.5; N, 14.9 per cent).

Its *semicarbazone* was prepared in the usual manner and was crystallised from alcohol as white needles, m. p.  $180^{\circ}$ . (Found: N, 28.8.  $C_{12}H_{15}ON_3$  requires N, 28.6 per cent).

*Removal of Nitrogen of the Pyrazoline Compound (VII, R=Me) and Formation of (IX, R=Me).*—Like the compound (VII, R=Ph), the pyrazoline derivative (4 g.) was heated for 3 hours and the resulting dark red coloured oil distilled at  $109^{\circ}/3$  mm. as a thin yellow liquid having a pleasant smell and turning brown on standing, yield 5 g. (Found: C, 81.8; H, 7.0.  $C_{11}H_{12}O$  requires C, 82.5; H, 7.5 per cent). It decolorises bromine in  $CCl_4$  and aqueous  $KMnO_4$  very readily.

Its *semicarbazone* was prepared in the usual manner and was crystallised from alcohol as fine needles, m. p.  $184^{\circ}$ . (Found: N, 19.8.  $C_{12}H_{15}ON_3$  requires N, 19.4 per cent).

*Hydrolysis of (IX, R=Me).*—The compound (1 g.) on boiling with strong hydrochloric acid for 2 hours and on steam distillation gave a small quantity of a liquid, which was characterised as acetophenone.

CHEMISTRY LABORATORY,  
HOLKAR COLLEGE, INDORE.

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## ANALYTICAL CHEMISTRY OF THORIUM. PART V. SEPARATION FROM CERITE EARTHS. CINNAMIC ACID

CH. VENKATESWARLU AND BH. S. V. RAGHAVA RAO

Cinnamic acid precipitates thorium completely from boiling solutions above the  $pH$  1.9. The precipitate, though flocculent in the beginning, collects on boiling and settles down quickly. Cerite earths in concentrations up to fifty-fold may be separated in a single operation in the  $pH$  range 2.0–2.6. Thorium in monazite extract, freed from zirconium and phosphate, has been accurately estimated at  $pH$  2.0 and 2.6.

Kolb and Ahrlé (*Z. angew. Chem.*, 1905, 18, 92) employed, amongst others, cinnamic acid for the precipitation of thorium, but abandoned the reagent in favour of *m*-nitrobenzoic acid. In this communication are reported the results of an extensive investigation on the use of cinnamic acid as a precipitant for thorium and as a reagent for the separation of rare earths therefrom; the only rare earths tried are the cerite earths occurring in the monazite. At  $pH$  1.9 and above, cinnamic acid gives a white voluminous precipitate with thorium which on boiling for a few minutes assumes a more crystalline form and settles quickly.

### EXPERIMENTAL

*Reagents Employed.*—The preparation of thorium nitrate solution and that of cerite earths is described in an earlier communication (this *Journal*, 1950, 27, 457). Cinnamic acid, B. D. H. reagent grade, was further purified by crystallisation from boiling water.

*Estimation.*—Thorium nitrate solution (10 ml.) was diluted to 100 ml. and heated to boiling. Boiling 0.5% cinnamic acid (100 ml.) was gradually added with stirring. The liquid was then boiled for 15 to 20 minutes during which time the flocculent precipitate of thorium cinnamate collected and settled down. It was filtered hot after 20 minutes through a 11 cm. Whatman No. 41 filter, washed with cold water and ignited wet to the oxide. For every 0.1 g. of thorium dioxide present 1 g. of the reagent was sufficient. Thorium dioxide obtained was 0.0624 g. Estimation by the *m*-nitrobenzoic acid method gave 0.0625 g. By this method as little as 0.0006 g. of thorium dioxide can be estimated accurately.

*Effect of  $pH$ .*—Since earlier reports (*loc. cit.*) rejected the reagent as unsatisfactory and the separation from other elements generally rests on a control of  $pH$ , the precipitation of thorium by the reagent under varying conditions of  $pH$  has been investigated. The results are given in Table I.

TABLE I

*Effect of  $p_H$  on the precipitation of thorium*ThO<sub>2</sub> taken = 0.0625 g. Total volume of the solution = 200 ml.

Expt. No.	$p_H$ of the final soln.	ThO <sub>2</sub> obtained.	Diff.	Expt. No.	$p_H$ of the final soln.	ThO <sub>2</sub> obtained.	Diff.
1	4.0	0.0625 g.	0.0 mg.	9	2.2	0.0624 g.	-0.1 mg.
2	3.6	0.0624	-0.1	10	2.0	0.0623	-0.2
3	3.4	0.0625	0.0	11	1.9	0.0624	-0.1
4	3.2	0.0626	+0.1	12	1.8	0.0618	-0.7
5	3.0	0.0624	-0.1	13	1.6	0.0610	-1.5
6	2.8	0.0625	0.0	14	1.5	0.0594	-3.1
7	2.6	0.0624	-0.1	15	1.4	0.0520	-10.5
8	2.4	0.0623	-0.2	16	1.25	0.0025	-60.0
				17	1.15	0.0000	-62.5

*Separation from Cerite Earths.*—The precipitation of thorium is not complete below  $p_H$  1.9 and the cerite earths are precipitated above 3.2. Even at  $p_H$  2.8 slight contamination of the thorium with cerite earths occurs. Preliminary investigations have shown that good results could be obtained in the  $p_H$  range 2.0 to 2.6. Two series of investigations, one at  $p_H$  2.0 and the other at  $p_H$  2.6, are reported in Table II.

TABLE II

ThO<sub>2</sub> taken = 0.0625 g.

Expt. No.	R <sub>2</sub> O <sub>3</sub> added (cerite earths)	ThO <sub>2</sub> obtained ( $p_H$ 2.0).	ThO <sub>2</sub> obtained ( $p_H$ 2.6).	Expt. No.	R <sub>2</sub> O <sub>3</sub> added (cerite earths).	ThO <sub>2</sub> obtained ( $p_H$ 2.0).	ThO <sub>2</sub> obtained ( $p_H$ 2.6).
1	0.064 g.	0.0624 g.	0.0625 g.	6	0.640 g.	0.0624 g.	0.0623 g.
2	0.128	0.0626	0.0625	7	1.280	0.0626	0.0623
3	0.256	0.0623	0.0624	8	1.920	0.0625	0.0626
4	0.320	0.0625	0.0624	9	2.560	0.0624	0.0627*
5	0.512	0.0625	0.0625	10	3.200	0.0627*	0.0630*

\* ThO<sub>2</sub> is slightly coloured.

Thus, a fifty-fold excess of cerite earths is removed in a single precipitation.

*Determination of Thorium in Monazite.*—Thorium in monazite extract, freed from zirconium and phosphate (cf. Part I, *loc. cit.*), was estimated with this reagent at  $p_H$  2.0 and 2.6. For comparison the results obtained after a double precipitation with *m*-nitrobenzoic acid are included in Table III.

TABLE III

*Estimation of monazite.*

Expt. No.	Vol of monazite extract taken.	<i>m</i> -Nitrobenzoic acid.	ThO <sub>2</sub> obtained with cinnamic acid at	
			pH 2.0.	pH 2.6.
1	10 g.	0.0650 g.	0.0650 g.	0.0648 g.
2	10	0.0650	0.0649	0.0650
3	20	0.1300	0.1302	0.1301
4	20	0.1300	0.1330	0.1299
5	1*	0.0065†	0.0066	0.0065
6	0.1*	0.00065†	0.0006	0.0007

† Theoretical.

\* A micro-pipette was employed.

*Composition of the Precipitate.*—Thorium cinnamate, precipitated as described above, has a slightly varying composition. Two different samples of the dried precipitate, weighing 0.1435 g. and 0.1272 g., gave on ignition 0.0492 g. and 0.0443 g. of ThO<sub>2</sub> respectively. These values indicate the association of three molecules of cinnamic acid with one thorium ion together with four molecules of water. It is not possible to weigh the precipitate directly, but ignition to the oxide is essential.

CHEMICAL LABORATORIES,  
ANDHRA UNIVERSITY,  
WALTAIR.

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"We gladly accede to the request of Dr. D. Chakravarti, Hon. Secretary of the Indian Chemical Society, to print the following letter addressed to us, and offer our sincere apologies for having misrepresented the practice of Indian chemists in publishing their papers :—

"On behalf of the Indian Chemical Society I beg to invite your kind attention to a statement on page 95, Vol. 74 (1950) of your esteemed Journal: "although the Indian Chemical Society has recently celebrated its Jubilee, most of the leading Indian chemists appear still to prefer the *Journal of the Chemical Society* to the *Journal of the Indian Chemical Society* as a medium for publication."

As a matter of fact Indian Students working in foreign countries sometimes find it convenient to publish their papers in the Journals of those countries. Authors of papers from India, except only one or two, seldom seek publication in foreign Journals.

I would request you, therefore, to publish this letter in your Journal by way of rectifying the misconception that has arisen out of the statement referred to above."

Ed.

## RESOLUTION OF *tris*-PHENYLBIGUANIDE COBALTIC CHLORIDE AND A STUDY OF THE KINETICS OF RACEMISATION OF THE LAEVO-GYRATE

BY SUNIL KUMAR SIDDHANTA, NIHAR KUMAR DUTT AND PRIYADARANJAN RÂY

Cobaltic *tris*-phenylbiguanide chloride was resolved through the fractionation of its chloro-*d*-tartrate, the less soluble *l*-chloro-*d*-tartrate separating out first with  $[M]_D^{32^\circ} = -285^\circ$ . From the mother-liquor *d*-chloro-*d*-tartrate was obtained with  $[M]_D^{32^\circ} = +290^\circ$ .

From the two diastereoisomerides the pure optically active components of the chloride, sulphate and nitrate of the complex base were obtained with  $[M]_D^{32^\circ} = \pm 2500^\circ$ ,  $\pm 2469^\circ$ ,  $\pm 2437^\circ$  respectively.

The velocity of inversion of the *l*-cobaltic *tris*-phenylbiguanide chloride and its temperature coefficient were measured, and the activation energy of its transformation was calculated from Arrhenius's equation. The value of its activation energy was found to be equal to 9700 calories approx. This is considerably lower than that of cobaltic *tris*-biguanide chloride (13,930 cal.), previously reported (Rây and Dutt, *J. Indian Chem. Soc.*, 1943, 20, 81).

Rây and Dutt (this *Journal*, 1941, 18, 289) resolved the cobaltic *tris*-biguanide chloride into its optically active enantiomerides. They also showed that a solution of the chloro-*d*-tartrate of the racemoid complex base exhibited the phenomenon of asymmetric transformation of the second order as described by Kuhn (*Ber.*, 1932, 65, 49). In order to study the effect of substitution in the ligand on the stability and the properties of the active forms of the complex, as also on the character of the diastereomerides through which the resolution is effected, the present work on the resolution of cobaltic *tris*-phenylbiguanide complex and the study of the kinetics of its racemisation was undertaken.

An account of the preparation and properties of cobaltic *tris*-phenylbiguanidine and its various salts has been given by Rây and Bhattacharya (this *Journal*, 1939, 16, 629). The resolution of this complex was effected, as in the case of *tris*-biguanide cobaltic complex, through the fractionation of its chloro-*d*-tartrate. The phenomenon of asymmetric transformation of the second order, which was observed during the progress of fractional crystallisation of the chloro-*d*-tartrate of the *tris*-biguanide complex, was not, however, found to occur in the present case. The two diastereomerides separated here normally from the solution on fractional crystallisation. As in the previous case, the laevo-gyrate, being less soluble, separated out first. This affords another evidence against Werner's generalisation regarding the comparative solubility of the chloro-*d*-tartrates of the optically active antipodes of cobaltic complexes (Werner, *Ber.*, 1912, 45, 865), which assumed that the *d*-chloro-*d*-tartrate of the cobaltic complexes should always form the less soluble variety (cf. also Jaeger, "Spatial Arrangement of Atomic Systems and Optical Activity", McGraw-Hill Book Co. Inc., 1930, p. 92). There is therefore no direct relationship between the space configuration of the molecules and their relative or absolute solubility.



From the two diastereoisomerides the pure optically active enantiomers of the chloride, sulphate and nitrate of the complex base were obtained with specific and molecular rotations of  $[\alpha]_D^{32} = \pm 337^\circ, \pm 300^\circ, \pm 315^\circ$ , and  $[M]_D^{32} = \pm 2500^\circ, \pm 2469^\circ$  and  $\pm 2437^\circ$  respectively. The corresponding molecular rotation values for chloride and nitrate of the complex cobaltic *tris*-ethylenediamine are:  $[M]_D = \pm 608^\circ$  and  $\pm 562^\circ$  respectively. A higher rotation value for the phenylbiguanide cobaltic complex, like that of the corresponding *tris*-biguanide complex, is indicative of a lower degree of symmetry of these complexes.

The active isomerides are quite stable in the solid state. In aqueous solutions they are fairly stable at lower temperatures, but begin, however, to racemise as the temperature rises. The velocity of racemisation of the pure active *l*-chloride has been measured and studied at different temperatures. From the temperature coefficient of the specific reaction rate, the activation energy for racemisation has been calculated. The results seem to support the mechanism of transformation suggested by Rây and Dutt (*loc. cit.*).

#### EXPERIMENTAL

The orange coloured crystals of *tris*-phenylbiguanide chloride were prepared and purified following the method described by Rây and Bhattacharya (*loc. cit.*). {Found: N, 28.01; Co, 8.04.  $[\text{Co}(\text{PhBigH})_3] \text{Cl}_3 \cdot 2.5\text{H}_2\text{O}$  requires N, 28.32; Co, 7.96 per cent}, where  $\text{PhBigH}$  = one molecule of phenylbiguanide =  $\text{C}_6\text{H}_5 \cdot \text{C}_2\text{N}_3\text{H}_6$ .

*r*-Cobaltic *tris*-phenylbiguanide chloro-*d*-tartrate was prepared by double decomposition from the cobaltic *tris*-phenylbiguanide chloride and one molecule of silver *d*-tartrate. The solution filtered from the silver chloride was evaporated to dryness on the water-bath. The crystals were left in air till their weight became constant. The substance forms reddish yellow microcrystalline solid, moderately soluble in water.

{Found: Cl, 4.01; Co, 6.57;  $\text{C}_4\text{H}_4\text{O}_6$ , 16.18.  $\left[ \text{Co}(\text{PhBigH})_3 \right] \text{Cl} \cdot \text{C}_4\text{H}_4\text{O}_6(d)$ ,  $7\text{H}_2\text{O}$  requires Cl, 3.95; Co, 6.56;  $\text{C}_4\text{H}_4\text{O}_6$ , 16.45 per cent}.

It loses all its water when kept in a vacuum desiccator over  $\text{H}_2\text{SO}_4$  (conc.).

*l*-Cobaltic *tris*-Phenylbiguanide chloro-*d*-tartrate.—The laevo component was obtained from the above described partial racemate in the form of bright yellow microcrystals by fractional crystallisation of the latter in aqueous solution. The rotation of the crystals was found to increase on repeated recrystallisation to a maximum value, when the crystals were finally washed first with cold water, then with alcohol, and afterwards dried in air. It is somewhat less soluble than the partial racemate. {Found:

Cl, 3.85; Co, 6.61;  $\text{C}_4\text{H}_4\text{O}_6$ , 16.22.  $l\text{-} \left[ \text{Co}(\text{PhBigH})_3 \right] \text{Cl} \cdot \text{C}_4\text{H}_4\text{O}_6(d)$ ,  $7\text{H}_2\text{O}$  requires Cl, 3.95; Co, 6.56;  $\text{C}_4\text{H}_4\text{O}_6$ , 16.45 per cent}.  $[\alpha]_D^{32} = -285^\circ$ ;  $[M]_D^{32} = -2564^\circ$ .

*d*-Cobaltic *tris*-Phenylbiguanide chloro-*d*-tartrate.—The mother-liquor from the laevo salt, described above, was treated with an excess of alcohol for complete pre-

cipitation. The crystals separated were dissolved in the least quantity of water and kept in a vacuum desiccator over  $\text{H}_2\text{SO}_4$  (conc.). A crop of impure laevo salt first separated out. This was removed and the filtrate in turn was subjected to the same treatment as before. The process was repeated with the more soluble fraction in each successive case until the rotation of the finally separated product became maximum and constant. This was washed and dried as usual. {Found: Cl, 3.81; Co, 6.48;  $\text{C}_4\text{H}_4\text{O}_6$ , 16.28.

$d\text{-}\left[\text{Co}(\text{PhBigH})_3\right]\text{Cl}$ ,  $7\text{H}_2\text{O}$  requires Cl, 3.95; Co, 6.56;  $\text{C}_4\text{H}_4\text{O}_6$ , 16.45 per cent}.

$[\alpha]_D^{32} = +290^\circ$ ;  $[M]_D^{32} = +2609^\circ$ .

*l-Cobaltic tris-phenylbiguanide sulphate* was obtained as an orange-red micro-crystalline solid from a solution of the laevo component of the complex chloro-*d*-tartrate by precipitation with a cold saturated solution of ammonium sulphate. The crystals were washed and dried as usual. {Found: Co, 7.14.  $l\text{-}[\text{Co}(\text{PhBigH})_3]_2(\text{SO}_4)_3$ ,  $10\text{H}_2\text{O}$  requires Co, 7.16 per cent}.  $[\alpha]_D^{32} = -300^\circ$ ;  $[M]_D^{32} = -4938^\circ$ .

*d-Cobaltic tris-phenylbiguanide sulphate* was obtained in the same manner as its laevo isomer from the corresponding *d*-chloro *d*-tartrate and ammonium sulphate. It is more soluble than its *l*-isomer. {Found: Co, 7.12.  $d\text{-}[\text{Co}(\text{PhBigH})_3]_2(\text{SO}_4)_3$ ,  $10\text{H}_2\text{O}$  requires Co, 7.16 per cent}.  $[\alpha]_D^{32} = +300^\circ$ ;  $[M]_D^{32} = +4938^\circ$ .

*l-Cobaltic tris-phenylbiguanide chloride* was obtained by double decomposition from the complex *l*-sulphate and barium chloride. The solution was then filtered from the precipitated barium sulphate and evaporated to dryness in a vacuum desiccator over  $\text{H}_2\text{SO}_4$  (conc.). The product was dried in air. {Found: Co, 8.08.  $l\text{-}[\text{Co}(\text{PhBigH})_3]\text{Cl}_3$ ,  $2.5\text{H}_2\text{O}$  requires Co, 7.97 per cent}.  $[\alpha]_D^{32} = -337^\circ$ ;  $[M]_D^{32} = -2500^\circ$ .

*d-Cobaltic tris-phenylbiguanide chloride* was prepared like its *l*-isomer from the corresponding *d*-sulphate and barium chloride. It has the same composition as the *l*-chloride. (Found: Co, 8.05. Calc. Co, 7.97 per cent).  $[\alpha]_D^{32} = +335^\circ$ ;  $[M]_D^{32} = +2485^\circ$ .

*l-Cobaltic tris-phenylbiguanide nitrate* was also obtained by double decomposition between the *l*-sulphate and barium nitrate. It is less soluble than the chloride. {Found: Co, 7.51.  $l\text{-}[\text{Co}(\text{PhBigH})_3](\text{NO}_3)_3$  requires Co, 7.60 per cent}.  $[\alpha]_D^{32} = -315^\circ$ ;  $[M]_D^{32} = -2437^\circ$ .

*d-Cobaltic tris-phenylbiguanide nitrate* was prepared like its *l*-isomer from the *d*-sulphate and barium nitrate. (Found: Co, 7.46. Calc. Co, 7.60 per cent).  $[\alpha]_D^{32} = +320^\circ$ ;  $[M]_D^{32} = +2483^\circ$ .

All measurements were made in a Franz Schmidt and Haensch polarimeter with a trisected field of vision and provided with an electrical heating arrangement by which the temperature could be maintained constant to  $\pm 0.1^\circ$ . A sodium vapour lamp was used as the source of illumination.

Cobalt was estimated as  $\text{CoSO}_4$  after decomposition of the substance with conc.  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . Tartaric acid was estimated by the iodate method (Goldenberg, *Z. anal. Chem.*, 1908, 87, 47; Unger and Haynes, *Analyst*, 1946, 71, 141).

*Kinetics of Racemisation*

The velocity constant of inversion,  $l\text{-salt} \rightleftharpoons d\text{-salt}$  for the active complex ion was deduced from the equation,

$$dx/dt = k(a-x) - kx = k(a-2x)$$

where  $a$  = initial conc. of the active salt;  $x$  = conc. of its optical antipode formed by inversion after a time  $t$ , and  $k$  = the velocity constant of inversion of the active forms.

$$\begin{aligned} \text{Integrating, } k &= \frac{1}{2t} \ln \frac{a}{(a-2x)} = \frac{2.303}{2t} \log \frac{a}{(a-2x)} \\ &= \frac{2.303}{2t} \log_{10} \frac{R_0}{R_t} \end{aligned}$$

where  $R_0$  = initial rotation,  $R_t$  = rotation after a time  $t$  in minutes.

$$\text{Hence, } T \text{ (halflife)} = \frac{2.303}{2k} \log_{10} 2.$$

The velocity constant was measured at  $46.2^\circ$  with solutions of different concentrations of the laevo-rotate with the following results.

TABLE I

I. Conc. (mol./litre) $\times 10^3 = 6.74$ .					
Time (min.)	...	0	180	360	540
$\alpha_D$	...	1.68	1.56	1.45	1.35
$k \times 10^4$	...	—	2.06	2.04	2.03
					Mean = 2.05
II. Conc. $\times 10^3 = 13.52$ .					
Time (min.)	...	0	180	360	540
$\alpha_D$	...	3.37	3.13	2.90	2.70
$k \times 10^4$	...	—	2.05	2.08	2.05
					Mean = 2.06
III. Conc. $\times 10^3 = 17.05$ .					
Time (min.)	...	0	180	360	540
$\alpha_D$	...	4.20	3.90	3.63	3.37
$k \times 10^4$	...	—	2.05	2.04	2.04
					Mean = 2.04

Therefore,  $k$  at  $46.2^\circ = 2.05$  (mean).

The results show that within the limits of the concentration employed the transformation is strictly of the monomolecular type. This is illustrated by plotting the logarithm of the rotation values against time in minutes, which gives straight lines as required by the equation. The velocity constant  $k$  can therefore be evaluated by multiplying the slope of the line by  $2.303/2$  (cf. Fig. 1).

For the measurement of temperature coefficient of the specific inversion rate an 1% solution of the *l*-gyrate in one dm. tube was used. The results are tabulated below

FIG. 1

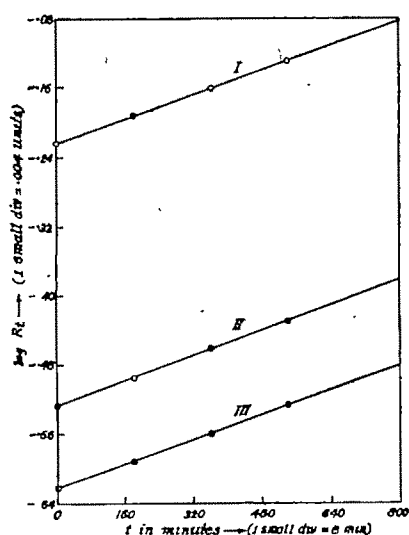
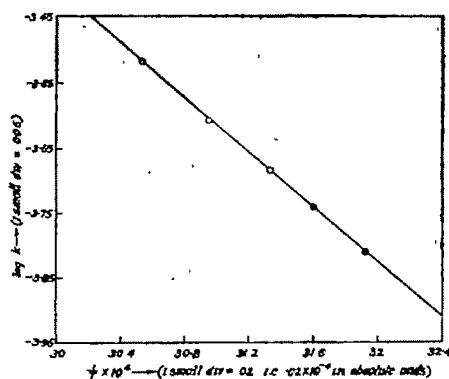


FIG. 2



and the Fig. 2 shows that a straight line is obtained by plotting the logarithm of the specific inversion rate against the reciprocal of the absolute temperature.

TABLE II

$t^\circ$	$1/T$	$k \times 10^4$	$\log k$	Half-life.
40.2°	0.003193	1.53	-3.815	37.75 hours
43.5°	0.003160	1.81	-3.742	31.92
46.2°	0.003133	2.05	-3.688	28.05
50.2°	0.003094	2.46	-3.609	23.50
54.6°	0.003053	3.05	-3.516	18.94

The activation energy for racemisation was then obtained from the slope of the line on the basis of Arrhenius's equation :

$$\frac{d \ln k}{dt} = \frac{E}{RT^2}, \text{ where } E = \text{the activation energy.}$$

$$\text{Integrating, } \log k = \frac{-E}{2.303 RT} + C (\text{constant})$$

$$\text{Or, } \log k_2/k_1 = \frac{E}{2.303 R} \times \frac{(T_2 - T_1)}{T_2 T_1} \text{ (between the limits } T_2 \text{ and } T_1 \text{)}$$

Expressed in the exponential form,  $k = s e^{-E/RT}$ , where  $s$  is the Arrhenius's constant.

The value of  $E$  is equal to 9640 calories as obtained from the slope of the curve, and 9720 calories from the integrated equation between the limits  $T_2$  and  $T_1$ .

When  $\log_{10} s$  is calculated from the value of  $E$ , it becomes equal to 1.13 only with  $k$  expressed in  $\text{sec}^{-1}$ . This is rather exceptionally low for a unimolecular reaction, which usually lies between 13 and 14. In the case of cobaltic *tris*-biguanide complex also a similar low value of 4.16 for  $\log_{10} s$  was observed for the inversion of its laevo enantiomorph (Rây and Dutt, *loc. cit.*). This indicates that the specific rate of inversion, or rather the probability factor  $P$  of Arrhenius's constant ( $s = PZ$ ), is unusually low in these cobaltic biguanide complexes; and much more so in the case of the phenylbiguanide complex. As already suggested in the earlier paper, the phenomenon may be attributed to an unusual delay in the specific energy transfer, which means an increase in the time lag between pre-activation and critical activation, or, as now expressed, between the formation of activated complex and its transformation, with the result that most of the activated molecules suffer deactivation before the change occurs. This time lag, and hence the chances of deactivation are likely to be greater in the case of the comparatively complicated and heavy molecules of the phenylbiguanide complex.

A comparative idea of the stability and optical properties of *l*-cobaltic *tris*-biguanide and *l*-cobaltic *tris*-phenylbiguanide chlorides can be obtained from the following values in Table III.

TABLE III

	$[M]^{23.2}$	$k \times 10^4$ (46.2°)	$T$ (half-life).	$E$ (calc.)	$\log_{10} s$
<i>l</i> -[Co(BigH) <sub>3</sub> ]Cl <sub>3</sub> ...	-2103°	2.46	23.5 hrs.	13930	4.16
<i>l</i> -[Co(PhBiH) <sub>3</sub> ]Cl <sub>3</sub> ...	-2500°	2.05	28.05	9700	1.13

Thus the substitution of a phenyl group in biguanide considerably increases its molecular rotation, but reduces its specific inversion rate and its activation energy. The value of Arrhenius's constant is also reduced to an exceedingly low value, nearly 27% of that for the *l*-cobaltic *tris*-biguanide complex, the latter itself being unusually low for a monomolecular reaction.

INORGANIC CHEMISTRY LABORATORY,  
UNIVERSITY COLLEGE OF SCIENCE,  
CALCUTTA.

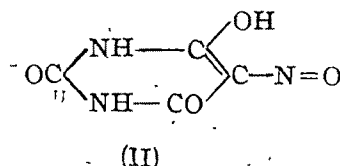
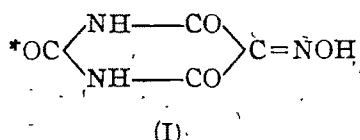
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## COLOUR IN RELATION TO THE CHEMICAL CONSTITUTION OF THE METALLIC DERIVATIVES OF *iso*NITROSOMALONYLGUANIDINE

By ROSHAN LAL HANDA AND SIKHIBHUSHAN DUTT

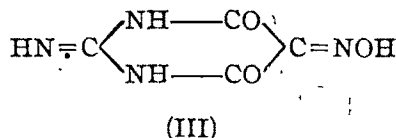
Metallic derivatives of *iso*nitrosomalonylguanidine have been prepared by the interaction of the potassium salt with various other metallic salts in aqueous solution. All the metallic derivatives prepared are brightly coloured substances having shades different from one another. Chemical analyses point to the existence of co-ordination compounds amongst these metallic derivatives.

*iso*Nitrosomalonylurea or violuric acid, which forms interesting pink coloured salts with organic and inorganic bases and dissolves in water to a pale pink solution, has been the subject of intensive study by Ghatak and Dutt (this *Journal*, 1928, 5, 665) who from the absorption spectra of these compounds have come to the conclusion that although the structure of violuric acid itself is the oximino-ketonic form (I), yet in the process of salt formation the nitroso-enolic structure (II) is produced by the migration of a hydrogen atom.

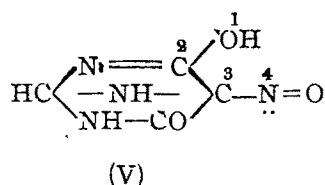
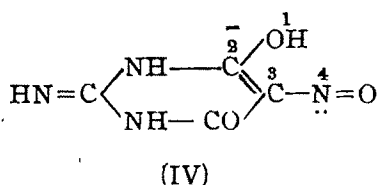


A similar behaviour was observed by Lal and Dutt (*Proc. Nat. Inst. Sci., India*, 1937, 3, 377) in the case of thiovioluric acid in which the oxygen atom in violuric acid marked with an asterisk had been replaced by a sulphur atom. This replacement was found to produce intensification in the colour of the salt to violet instead of pink, due to increased load in juxtaposition to the chromophore.

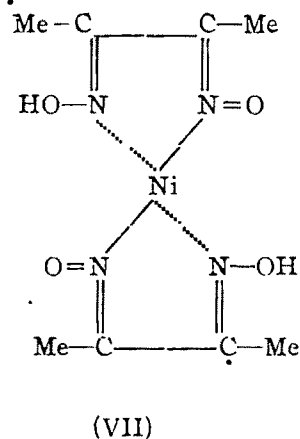
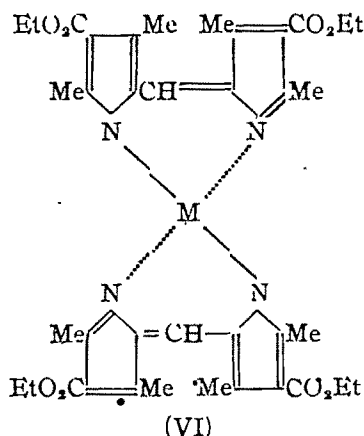
*iso*Nitrosomalonylguanidine (III)



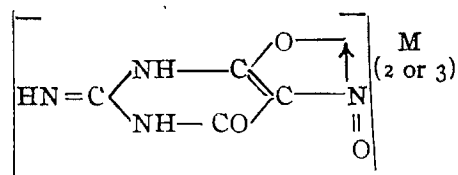
which is structurally very closely related to violuric and thiovioluric acid has been found to yield intensely coloured salt with organic and inorganic bases, the organic salts having been already prepared and described by Dass and Dutt (*Proc. Nat. Acad. Sci.*, 1939, 9, 93). The inorganic salts of this interesting compound form the subject of the present investigation. While the organic salts have been found to exhibit mainly violet colour in aqueous solution, the inorganic salts have a wide range of colour from yellow and pink to dark blue and green. From the point of view of analogy of violuric and thiovioluric acids, the metallic salts of *iso*nitrosomalonylguanidine should correspond to the nitroso-enolic structure of this substance which may have two alternative forms (IV, V):



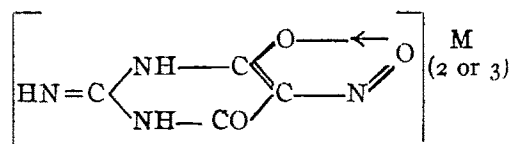
Theoretical considerations show that in either of these forms the metallic salts of isonitrosomalonylguanidine are probably of the nature of internally complex compounds. The acid molecule in its nitroso-enolic form contains one replaceable hydrogen atom which can be replaced by the metal atom during salt formation. The possibility of inner complex salt formation arises whenever acidic and donor functions (such as amino, carbonyl, etc groups) are suitably placed in the same molecule, i.e., in 1:4 or 1:5 positions to one another. The molecule of isonitrosomalonylguanidine contains a nitrogen atom in 1:4 position to the replaceable hydrogen atom and has got one lone pair of electrons. By virtue of this lone pair of electrons, the nitrogen atom can act as a donor and form a co-ordinate link with the metal atom, for which the electrons are supplied by the nitrogen atom. The co-ordinating power of the nitrogen atom is well known in the complex amines of cobalt and other metals and a large number of other co-ordination compounds. That chelation can take place readily when the two atoms concerned in chelation are in 1:4 position is also a well known fact. Another peculiar feature about these compounds is that in some cases the tendency of the metal atom to acquire the most stable co-ordination number is over-ridden by the valency requirements of the metal atom concerned. In view of the fact that the molecule of isonitrosomalonylguanidine contains a replaceable hydrogen atom, the number of molecules of the acid which will react with one atom of the metal will be equal to the valency of the metal. The acid molecule as a whole acts as a bidentate chelate radical and thus the co ordination number of the metal atom will be equal to twice its valency. This sort of behaviour is exemplified by other co-ordination compounds whose structures are well known, e.g., the cobalt salt of ethyl tetramethylpyrromethane-4:4'-dicarboxylate (VI) (*J. Chem. Soc.*, 1938, 368) and dimethylglyoxime complex of nickel (VII).



That the metallic derivatives of *isonitrosomalonylguanidine* are of the nature of inner complexes is further supported by the fact that the salts are very stable. Moreover, their insolubility in water and solubility in organic solvents also support this view. The salts do not possess such high melting points as true salts, which is also in favour of the suggestion that they are of the nature of co-ordination compounds. The salts of bi- and tri-valent metals may thus be given the following general formula where M is the metal atom (VIII).



Alternatively they may also be formulated as shown below (IX) whereby a six-membered ring may be formed:



#### EXPERIMENTAL

*isoNitrosomalonylguanidine* was prepared according to the method given by Dass and Dutt (*loc. cit.*). The potassium salt of the compound was prepared in the following way: *isoNitrosomalonylguanidine* (15.6 g.) was ground up into a thick cream with water (50 c.c.) and the whole converted into an almost clear, crimson solution by the addition of a 20% aqueous solution of potassium hydroxide (30 c.c.). After filtering, the solution was treated with an excess of rectified spirit (95%, 350 c.c.), when the potassium salt was gradually deposited in the form of glistening violet needles. After keeping in the refrigerator overnight, the product was filtered off, washed with cold rectified spirit (150 c.c.) and ether (50 c.c.) and dried in the air-oven at 70°. Yield of the potassium salt corresponded to nearly 95% of the theoretical (18.6 g.).

For the preparation of the metallic derivatives, the aqueous or aqueous-alcoholic solution of the salt of the metal (the chloride or the nitrate, whichever was more soluble) was gradually added to a 10% aqueous solution of the potassium salt of *isonitrosomalonylguanidine*, until the former was in slight excess. The metallic derivative was immediately precipitated in fine crystalline form which very often took the shape of glistening prismatic needles. This was filtered off, washed with aqueous alcohol and then with pure alcohol and dried. The yields of the salts in most cases were practically quantitative and in no case less than 90% of the theoretical calculated on the basis of the potassium salt of *isonitrosomalonylguanidine* employed. In a few cases the salts were soluble in some organic solvents (chiefly acetone) and could be recrystallised from them. But in many cases this could not be done as they were found to be insoluble in



all organic solvents. As prepared, however, the salts were found to be quite pure and yielded fairly good analytical data. It was noted that all the metallic derivatives of isonitrosomalonylguanidine described in this paper have different colours. They all melt with decomposition at comparatively low temperatures. For the sake of abbreviation, the experimental details have been summarised in Table I.

TABLE I

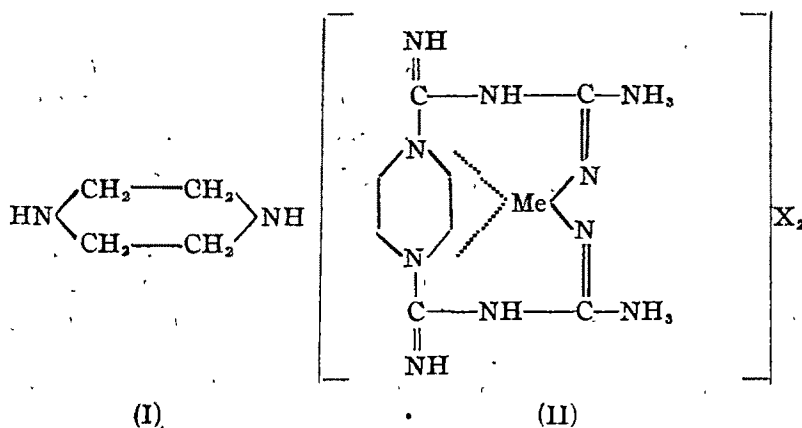
Compound	Colour.	Decomp point	Solvent from which crystallised.	Metal		Nitrogen	
				found.	calc.	found.	calc.
K	Deep violet	192°	Hot water, purple colour in soln.	19.95%	20.1%	28.767%	28.87%
Li	Deep pink	205°	Acetone; pink colour in soln.	4.268	4.292	33.79	34.58
Ca	Pinkish yellow	218°	Could not be obtained in soln.	28.16	27.949	26.53	26.05
Ba	Red	235°	"	46.67	46.98	16.45	16.25
Mg	Pale yellow	226°	"	19.15	19.05	29.23	26.82
Zn	Dirty white	260°	"	39.17	38.75	22.64	22.12
Cd	Yellowish white	235°	"	26.79	26.62	26.41	26.52
Hg	Yellowish brown	254°	"	66.1	66.0	11.95	12.28
Al	Grey	210°	"	5.539	5.488	33.83	34.14
Pb	White	196°	"	40.5	40.06	21.24	21.67
Bi	Light blue	206°	Acetone; light purple colour in soln.	31.59	31.01	24.59	24.95
Mn	Deep chocolate	258°	Could not be obtained in soln.	34.53	34.71	23.81	23.59
Co	Snuff-coloured	245°	"	36.6	36.39	22.92	23.04
Ni	Dark green	225°	"	36.47	36.43	22.98	23.04
Ferrous	Deep blue	225°	"	35.3	35.081	23.57	23.49
Ferric	Bluish green	220°	"	26.35	26.53	25.96	26.54
Cu	Dark green	214°	"	50.16	50.63	17.44	17.83
U	Deep yellow	191°	"	71.6	69.72	10.54	10.93
Ce	Light brown	Does not decompose up to 300°	"	47.82	48.58	18.48	18.99
Th	Dirty brown	220°	"	50.42	49.96	17.92	18.08

# COMPLEX COMPOUNDS OF BIGUANIDE WITH BIVALENT METALS. PART XII. COPPER AND NICKEL PIPERAZINE DIBIGUANIDE AND THEIR SALTS

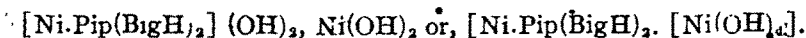
BY PRIYADARANJAN RÂY AND AJOY KUMAR CHOUDHURY

Piperazine dibiguanide, prepared from piperazine and dicyandiamide, has been found to act as a quadridentate group, furnishing four points of attachment to a central metal atom with the formation of metal-biguanide complexes of the inner metallic type. Preparation and properties of cupric piperazine dibiguanide hydroxide, its chloride, sulphate and nitrate, as well as of nickel piperazine dibiguanide hydroxide, its chloride and sulphate, besides of a dinickel piperazine dibiguanide hydroxide, have been described. The constitution of the last named compound has also been discussed.

Piperazine dibiguanide was prepared by condensing piperazine (I) with dicyandiamide. This was found to serve as a quadridentate molecule supplying four points of attachment to a central metal atom like Cu or Ni, giving rise to inner metallic complexes of ethylene dibiguanide type (II).



With nickel salts in strongly alkaline medium a yellow coloured nickel piperazine dibiguanide base was obtained, having the composition,  $\text{Ni}_2[\text{C}_4\text{H}_8\text{N}_2(\text{BigH})_2](\text{OH})_4 \cdot 5\text{H}_2\text{O}$ , where  $\text{C}_4\text{H}_8\text{N}_2(\text{BigH})_2$  is a molecule of piperazine dibiguanide. The substance gives a paramagnetic moment of  $2.48\mu_B$ , unlike the other nickel complexes with the same ligand, which are all diamagnetic, a property characteristic of all planar nickel complexes with hybrid  $dsp^2$  bonds. This is best accounted for by the following representation of its configuration as a compound of nickel piperazine dibiguanide hydroxide with nickel hydroxide. It is also supported by the result of dehydration at  $110^\circ$ , when the substance loses five molecules of water.



$\text{Pip}(\text{BigH})_2$  = a molecule of piperazine dibiguanide.

The nickel in nickel piperazine dibiguanide being diamagnetic as usual, while the nickel atom in  $\text{Ni}(\text{OH})_2$  or in  $\text{Ni}(\text{OH})_4$  giving a paramagnetic moment ( $2.8 \mu_B$  - theor.) characteristic of ionic nickel, the moment value for the complex compound as a whole should be equal to that of the latter. This is more or less in agreement with the observed value of  $2.48 \mu_B$ .

## EXPERIMENTAL

*Piperazine Dibiguanide Sulphate*.—Piperazine (4.3 g.) and dicyandiamide (8.4 g.) were heated with about 75 c.c. of water in a conical flask on the water-bath for about 3 hours with occasional additions of 5 c.c. of copper sulphate solution (10 g. in 30 c.c. water) at intervals of 20 minutes. To the resulting mixture, a solution of NaOH (2.8 g.) was added, and the heating was continued till the mixture turned red. This was cooled and filtered; and the red residue was then decomposed with sulphuric acid (1:3), when the white piperazine dibiguanide sulphate separated out gradually on cooling. This was filtered and washed with cold water until free from copper. The product was then dissolved in ammonia and a little NaOH, the mixture filtered and acidified with dilute sulphuric acid (1:1). On cooling, shining white crystals of piperazine dibiguanide sulphate separated out from the solution. These were filtered, washed with cold water and dried in air. (Found: N, 29.40; S, 13.37.  $\text{C}_8\text{H}_{18}\text{N}_{10} \cdot 2\text{H}_2\text{SO}_4 \cdot 1.5\text{H}_2\text{O}$  requires N, 29.35; S, 13.41 per cent).

*Copper Piperazine-dibiguanide Hydroxide*.—Piperazine dibiguanide sulphate (4.7 g.), dissolved in ammonia and a little caustic soda solution (about 20 c.c. of 2N-NaOH), was treated with an ammoniacal solution of copper sulphate (1.6 g.) with constant stirring. The precipitate of red-violet copper piperazine dibiguanide hydroxide, which separated immediately, was filtered and washed with cold water till free from sulphate. The product was dried in a desiccator to a constant weight. {Found: Cu, 15.46; N, 34.80;  $\text{H}_2\text{O}$  (by loss at  $105^\circ$ ), 21.97.  $[\text{Cu.Pip}(\text{BigH})_2](\text{OH})_2 \cdot 3\text{H}_2\text{O}$  requires Cu, 15.60; N, 34.50;  $\text{H}_2\text{O}$ , 22.10 per cent}. [Found (anhydrous compound): Cu, 20.07; N, 44.31. Calc. Cu, 20.10; N, 44.30 per cent].

The substance forms red-violet powder, insoluble in water and alcohol. When heated with solutions of ammonium salts, it liberates ammonia. It is readily decomposed by dilute acids.

*Copper piperazine-dibiguanide chloride* was obtained as a red-violet residue when the complex copper base was heated with a solution of ammonium chloride on the water-bath until the evolution of ammonia ceased. The product was filtered, washed with cold water and dried in air. The substance is sparingly soluble in hot water and practically insoluble in alcohol. {Found: Cu, 13.69; Cl, 15.42;  $\text{H}_2\text{O}$  (by loss at  $105^\circ$ ), 15.55.  $[\text{Cu.Pip}(\text{BigH})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  requires Cu, 13.70; Cl, 15.40;  $\text{H}_2\text{O}$ , 15.60 per cent}. [Found (anhydrous compound): Cu, 16.39; Cl, 18.28. Calc. Cu, 16.34; Cl, 18.27 per cent].

The *complex sulphate* was obtained as a violet compound from the complex base and ammonium sulphate solution in the same way as the complex chloride. The substance is insoluble in water and alcohol. {Found: Cu, 12.57; S, 6.15;  $\text{H}_2\text{O}$ , (by loss

at 105°), 19.29.  $[\text{Cu.Pip}(\text{BigH})_2]\text{SO}_4 \cdot 5.5\text{H}_2\text{O}$  requires Cu, 12.40; S, 6.20;  $\text{H}_2\text{O}$ , 19.31 per cent}. The anhydrous sulphate gives Cu, 15.40; S, 7.72. Calc. Cu, 15.30; S, 7.73 per cent.

The *complex nitrate* was prepared from the complex base and a solution of ammonium nitrate, as described in the previous cases. The substance forms red powder, insoluble in water and alcohol.

{Found: Cu, 13.70;  $\text{H}_2\text{O}$  (by loss at 100°), 3.88.  $[\text{Cu.Pip}(\text{BigH})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  requires Cu, 13.80;  $\text{H}_2\text{O}$ , 3.90 per cent}. [Found (anhydrous compound): Cu, 14.39. Calc. Cu, 14.39 per cent].

*Nickel piperazine-dibiguanide nickel hydroxide* was obtained as a buff coloured precipitate by adding an ammoniacal solution of nickel sulphate to that of piperazine dibiguanide sulphate in presence of an excess of caustic soda. The product was filtered, washed well with cold water and dried in a desiccator to a constant weight, when the colour of the substance changed to yellow. The substance is insoluble in water and alcohol, and liberates ammonia from ammonium salt solution. {Found: Ni, 21.93; N, 26.40;  $\text{H}_2\text{O}$  (by loss at 110°), 16.80.  $[\text{Ni.Pip}(\text{BigH})_2](\text{OH})_2 \cdot \text{Ni}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  requires Ni, 22.17; N, 26.40;  $\text{H}_2\text{O}$ , 17.00 per cent}. [Found (anhydrous compound): Ni, 26.52; N, 31.85. Calc. Ni, 26.70; N, 31.80 per cent].

*Nickel piperazine-dibiguanide chloride* was obtained as an insoluble orange-yellow product by heating the complex nickel base, described above, with a solution of ammonium chloride on the water-bath until the evolution of ammonia ceased. The product was washed with cold water and dried in air to a constant weight. {Found: Ni, 11.34; N, 27.22; Cl, 13.48;  $\text{H}_2\text{O}$  (by loss at 110°), 25.88.  $[\text{Ni.Pip}(\text{BigH})_2]\text{Cl}_2 \cdot 7.5\text{H}_2\text{O}$  requires Ni, 11.31; N, 27.00; Cl, 13.60;  $\text{H}_2\text{O}$ , 26.00 per cent}. [Found (anhydrous compound): Ni, 15.19; Cl, 18.49. Calc. Ni, 15.20; Cl, 18.50 per cent].

*Nickel piperazine-dibiguanide hydroxide base* was obtained as an insoluble orange coloured product by keeping the complex nickel chloride (1 mol.) in contact with a solution of caustic soda (2 mol.) for two days and then heating the mixture on the water-bath for some time. The product was washed with cold water and dried in a desiccator to a constant weight. {Found: Ni, 15.56; N, 37.33;  $\text{H}_2\text{O}$  (by loss at 105°), 16.70.  $[\text{Ni.Pip}(\text{BigH})_2](\text{OH})_2 \cdot 1.5\text{H}_2\text{O}$  requires Ni, 15.70; N, 37.46;  $\text{H}_2\text{O}$ , 16.80 per cent}. Found (anhydrous compound): Ni, 18.88; N, 44.77. Calc. Ni, 18.90; N, 45.05 per cent].

*Nickel piperazine-dibiguanide sulphate* was prepared by adding an ammoniacal solution of nickel sulphate (1 mol.) to a slightly ammoniacal solution of piperazine dibiguanide sulphate (1 mol.), and then heating the mixture on the water-bath until the solution was practically free from ammonia. The insoluble orange coloured product was filtered, washed with cold water and then dried in air to a constant weight. It can also be obtained by heating the complex nickel base with a solution of ammonium sulphate. {Found: Ni, 12.05; N, 28.46; S, 6.68;  $\text{H}_2\text{O}$  (by loss at 105°), 16.40.  $[\text{Ni.Pip}(\text{BigH})_2]\text{SO}_4 \cdot 4.5\text{H}_2\text{O}$  requires Ni, 11.90; N, 28.50; S, 6.53;  $\text{H}_2\text{O}$ , 16.54 per cent}. [Found (anhydrous compound): Ni, 14.34; N, 34.31. Calc. Ni, 14.36; N, 34.20 per cent].

*Magnetic Susceptibilities.*—The magnetic susceptibilities of some of the compounds described above, were measured in a Gouy's balance, and the results are given below.

Substance	$\chi_g$	$\chi_g$ (obs.)	$\delta$ (diamagnetic correction)	$\chi_M$ (corr.)	$\mu_B$
1. Cu Pip(BigH <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> , 4H <sub>2</sub> O	$2.61 \times 10^{-6}$	$1204 \times 10^{-6}$	$222 \times 10^{-6}$	$1426 \times 10^{-6}$	1.87
2. [Ni.Pip(BigH <sub>2</sub> ) <sub>2</sub> ][Ni(OH) <sub>2</sub> ], 5H <sub>2</sub> O	4.31 „	2284 „	217 „	2501 „	2.48
3. [Ni.Pip(BigH <sub>2</sub> ) <sub>2</sub> ]Cl <sub>2</sub> , 7.5H <sub>2</sub> O	Diamagnetic.				

INORGANIC CHEMISTRY LABORATORY,  
UNIVERSITY COLLEGE OF SCIENCE,  
CALCUTTA.

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## STUDIES ON ENZYME LIPASE. COMPARATIVE STUDY OF LIPASES FROM OIL SEED CAKES

By C. V. RAMAKRISHNAN AND B. N. BANERJEE

Lipases are obtained from different oil seed cakes like ghani cake, propeller cake and pressed cake and it is found that generally in all cases, the activity is low but out of the three, the activity decreases in the order: pressed, ghani and propeller cake lipase. Ghani cake lipase being cheaper and moderately active has been used for further experiments.

With respect to the effect of the nature of the buffer, substrate and the lipase it is found that the optimum  $p_H$  is generally on the acidic side and the change in the optimum  $p_H$  is not much with the nature of the buffer but is slight with the nature of the substrate. The castor and groundnut samples are the best active, groundnut oil is the best substrate and sodium acetate-acetic acid buffer is the best buffer.

Optimum buffer concentration and optimum substrate concentration depend upon the nature of the lipase and the percentage hydrolysis of the oil goes on increasing with the enzyme concentration. The optimum temperature for the enzymic hydrolysis of the oil by cake lipase is  $37^{\circ}$ – $40^{\circ}$ .

Generally organic salts like glycine, ascorbic acid, etc. accelerate the lipase activity to a greater extent and  $MnSO_4$  and ammonium phosphate from inorganic salts also possess greater accelerating power.

The activity of petroleum ether-dried sample slowly decreases on ageing. The acetone-drained sample keeps its activity fairly constant even though it is low.

Ramakrishnan and Nevgi (M.Sc. Thesis, Bombay University, 1947) have carried out a general study on the lipases obtained from different oil seeds. In the present work an attempt has been made to investigate oil seed cakes to obtain cheaper and active variety of lipase from them. An experiment was conducted with the following oil seed cakes to study their lipolytic activity: (1) Castor cake (*Ricinus communis*), (2) Groundnut cake (*Arachis hypogea*); (3) Sesame cake (*Sesamum indicum*); (4) Mysore seed cake (*Guizotia abyssinica*), (5) Mustard cake (*Brassica nigra*), (6) Safflower cake (*carthamus*) and (7) Cottonseed cake (*Gossypium herbiceum*).

### EXPERIMENTAL

*Nature of the Oil Cake.*—The first factor to be considered is the type of the oil cake to be chosen for the experiment. There are three types of oil cakes available—oil cake from cold drawn press method, oil cake from *ghani* method and oil cake from propeller method. These three oil cakes were taken and lipases prepared from them according to Longnecker and Haly's method (*J. Amer. Chem. Soc.*, 1935, **57**, 2019) and tested for their activities. The hydrolysis of groundnut oil by these lipases was studied.

Each experiment consisted of groundnut oil (1 c.c.), water (5 c.c.) and cake lipase (0.1 g.) in a test tube and kept in the incubator for 24 hours at  $37^{\circ}$ . Then the contents were removed and titrated against  $N/10$  sodium hydroxide after the addition of neutral alcohol (25 c.c.) and warming for sometime. Always a blank accompanied the sample. Necessary precautions were taken to take readings under sterile conditions. The difference between the sample and the blank gives the activity of the lipase in terms of c.c. of  $N/10$  sodium hydroxide. The results are shown in Table I.

TABLE I

Oil cake : Groundnut oil.

Set No.	Source of lipase.	Diff. bet the sample & the blank in terms of c.c. of $N/10$ - NaOH for					
		Castor.	Ground-nut.	Seasame.	Mysore seed.	Safflower.	Mustard seed cake.
1	Cold pressed cake	0.5	0.4	0.8	0.5	0.9	0.5
2	Ghani cake	0.3	0.2	0.5	0.3	0.6	0.4
3	Propeller cake	0.1	0.1	0.2	0.1	0.3	0.7

It appears from Table I that the activity is most in cold pressed cake lipase, least in propeller cake, and moderate in ghani cake. Out of the three, ghani cake is the most suitable since its changes are moderate and it is available in plenty if the new method of extracting oil suggested by Banerjee and Ramanamurti (*Ind. J. Med Res.*, 1948, 36, 4) is developed in the country. Hence, for further experiments ghani cake was chosen.

#### *Different Factors controlling the Activity of Cake Lipase*

It has been observed that the cake lipases are not very reactive. These cannot be used for fat splitting on an industrial scale unless they show appreciable activity. Hence different factors like H-ion concentration, nature of the buffer, substrate and lipase, effect of buffer, substrate and enzyme concentrations, effect of salts, temperature, etc. on the activity of the cake lipase are to be studied in order to find out the optimum conditions for their maximum activity.

The ghani cakes of different oil seeds were powdered well and packed in a filter paper and soxhleted with low boiling petroleum ether for about 3 hours till the oil was completely removed. The packet was taken out, the extracted mass spread over a long sheet of filter paper, dried completely free from petroleum ether at room temperature, sieved through a 60 mesh sieve and the fine powder so obtained was preserved in a bottle after adding a few drops of toluene to prevent bacterial growth and used for further experiments.

*Effect of the Nature of the Buffer, Substrate and Lipase on the Activity of Cake Lipase.*—Disodium Phosphate-citric acid buffer mixtures of different  $p_H$  were prepared according to McIlvaine's method (*Biochem. J.*, 1929, 49, 183), sodium acetate—hydrochloric acid and sodium acetate—acetic acid buffer mixtures of different  $p_H$  were prepared according to Walpole's method (*J. Biol. Chem.*, 1914, 105, 2501). The buffer mixtures were tested for their respective  $p_H$  and, if necessary, adjusted by addition of any of the constituents of the buffer mixtures. The above buffer mixtures were used in the following experiments.

The hydrolysis of different freshly prepared oils were carried out using the three buffers and different cake lipases.

Each set of the experiments consisted of the oil (1 c.c.), water (5 c.c.), cake lipase (0.1 g.) and 2 c.c. of buffer mixtures of varying  $p_H$  value and a few drops of toluene in a test tube, corked well, and incubated for 24 hours at 37°. Always a blank accom-

panied each sample. After the period of incubation, each test tube was taken out and the contents titrated against  $N/10$  sodium hydroxide after adding 25 c.c. of neutral alcohol and warming for sometime. Necessary precautions were taken to take the readings under sterile conditions. The difference between the sample and the blank gives the activity of the lipase in terms of c.c. of  $N/10$  sodium hydroxide. The results are shown in Tables III and IV.

The combined results for the hydrolysis of the different oils by different cake lipases using disodium phosphate-citric acid buffer with special reference to the optimum  $p_H$  are shown in Table III.

TABLE II

Buffer : Disodium phosphate-citric acid.

Difference in c.c. of  $N/10$ -NaOH between the sample and the blank in case of

Set No.  $p_H$ . Castor. Ground-nut. Sesame, Mysore. Safflower. Mustard. Cotton seed.

Groundnut oil = 1 c.c. F.F.A. = 0.05 c.c. of  $N/10$ -NaOH for 1 c.c. of oil. Sap. value = 188. I.V. = 100.1.

1	2.8	2.8	3.2	2.7	2.5	2.6	3.7	2.5
2	3.2	3.2	3.7	3.0	2.6	2.9	4.1	2.7
3	3.6	3.9	4.0	3.2	3.0	3.1	5.0	3.0
4	3.8	5.2	4.4	4.4	3.3	3.5	4.2	3.2
5	4.4	3.8	5.3	3.0	3.8	3.9	3.9	3.0
6	4.8	3.2	4.9	2.8	4.6	4.2	3.6	2.7
7	5.2	3.0	4.5	2.4	4.8	4.5	3.1	2.3
8	5.9	2.7	4.1	2.1	4.0	4.1	2.7	2.1
9	6.2	2.5	3.8	1.8	3.7	3.8	2.4	1.8
10	7.2	2.1	3.5	1.5	3.2	3.2	2.1	1.5

Sesame oil = 1 c.c. F.F.A. = 0.05 c.c. Sap. value = 189.3. I.V. = 114.2.

1	2.8	4.0	4.1	4.3	3.1	2.2	3.9	2.7
2	3.2	4.2	4.3	4.5	3.3	2.6	4.2	2.9
3	3.6	4.5	4.6	4.9	3.7	2.9	4.5	3.1
4	3.8	5.0	4.8	4.6	4.0	3.2	4.8	2.8
5	4.4	4.6	5.1	4.3	4.3	3.6	4.3	2.5
6	4.8	4.2	4.4	4.0	3.9	3.8	4.0	2.3
7	5.2	4.0	4.0	3.7	3.6	3.8	4.0	2.3
8	5.9	3.8	3.6	3.3	3.4	3.9	3.4	1.8
9	6.2	2.5	3.8	3.0	3.1	3.5	3.1	1.5
10	7.2	3.1	3.0	2.7	2.9	3.2	2.8	1.2



TABLE II (contd.)

Difference in c.c. of  $N/10$ -NaOH between the sample & the blank in case ofSet. No.  $pH$  Castor G. nut Sesame. Mysore. Safflower Mustard. Cottonseed.

Castor oil = 1 c.c. F.F.A. = 0.30 c.c. Sap. value = 176.7. IV = 83.7.

1	2.8	5.5	2.6	1.9	1.3	1.5	1.9	2.1
2	3.2	5.8	2.9	2.1	1.6	1.8	2.2	2.4
3	3.6	6.1	3.1	2.5	1.9	2.1	2.5	2.7
4	3.8	5.7	3.4	2.8	2.1	2.5	2.9	2.3
5	4.4	5.3	3.8	3.1	2.4	2.7	2.6	2.0
6	4.8	5.0	3.5	2.9	2.8	3.0	2.3	1.8
7	5.2	4.7	3.2	2.6	2.1	3.2	2.1	1.5
8	5.9	4.2	3.0	2.3	1.8	2.9	1.9	1.3
9	6.2	3.9	2.7	2.0	1.5	2.6	1.6	1.0
10	7.2	3.6	2.3	1.0	1.2	2.4	1.2	0.7

Mysore seed oil = 1 c.c. F.F.A. = 0.05 c.c. Sap. value = 185.6. I.V. = 118.6.

1	2.8	3.9	2.5	3.3	3.0	3.0	3.6	1.4
2	3.2	4.2	2.8	3.5	3.3	2.6	4.0	1.8
3	3.6	4.7	3.0	3.8	3.7	2.9	4.3	2.1
4	3.8	4.5	3.1	4.1	4.2	3.2	3.9	2.9
5	4.4	4.4	3.2	3.9	4.6	3.6	3.7	2.6
6	4.8	4.1	5.5	3.6	5.0	3.8	3.4	2.3
7	5.2	3.8	3.1	3.2	4.7	4.1	3.1	2.0
8	5.9	3.5	2.9	3.0	4.3	3.9	2.7	1.7
9	6.2	3.0	2.7	2.8	4.0	3.6	2.4	1.4
10	7.2	2.7	2.2	2.4	3.8	3.2	2.0	1.1

Safflower oil = 1 c.c. F.F.A. = 0.03 c.c. Sap. value = 187.2. I.V. = 143.4.

1	2.8	3.1	3.7	2.9	2.8	3.2	3.1	1.8
2	3.2	3.7	4.1	3.2	3.1	3.4	3.3	2.2
3	3.6	4.0	4.5	3.7	3.5	3.7	3.6	2.7
4	3.8	4.3	4.8	3.4	3.8	4.1	4.0	2.4
5	4.4	4.1	5.1	3.1	4.0	4.4	3.8	2.0
6	4.8	3.8	4.6	2.8	4.3	4.9	3.5	1.8
7	5.2	3.5	4.2	2.5	4.8	5.2	3.2	1.5
8	5.9	3.1	3.8	2.3	4.4	4.7	3.0	1.1
9	6.2	2.7	3.2	2.0	4.0	4.2	2.7	0.8
10	7.2	2.3	3.0	1.7	3.6	3.8	2.3	0.5

TABLE II (contd.)

Difference in c.c. of $N/10$ -NaOH between the sample and the blank in case of								
Set No.	$p_H$	Castor.	G. nut.	Seasame.	Mysore.	Safflower.	Mustard.	Cottonseed
Mustard oil=1 c.c. F.F.A.=0.10 c.c. Sap. value=174.4. I. V.=106.8.								
1	2.8	3.5	3.2	2.3	3.3	2.3	4.3	1.5
2	3.2	3.8	3.4	2.5	3.5	2.7	4.8	1.7
3	3.6	4.1	3.7	2.9	3.7	3.0	5.2	2.0
4	3.8	3.9	4.0	3.2	4.0	3.5	6.4	2.3
5	4.4	3.7	4.2	3.0	4.2	3.9	5.9	2.1
6	4.8	3.4	4.7	2.7	4.5	3.4	5.4	1.8
7	5.2	3.1	4.3	2.5	4.1	3.1	5.1	1.3
8	5.9	2.8	4.1	2.2	3.8	2.7	4.8	1.0
9	6.2	2.5	3.8	1.9	3.5	2.3	4.5	0.7
10	7.2	2.2	3.3	1.6	3.2	2.0	4.2	0.4
Cottonseed oil=1 c.c. F.F.A.=0.10 c.c. Sap. value=154.5 I. V.=113.2.								
1	2.8	2.1	1.9	2.1	1.3	0.9	1.5	2.5
2	3.2	2.5	2.3	2.4	1.5	1.2	1.8	2.9
3	3.6	3.0	2.7	2.6	1.6	1.5	2.1	3.2
4	3.8	3.3	3.0	2.9	1.9	1.8	2.4	3.5
5	4.4	3.1	3.2	2.7	2.1	2.1	2.2	3.1
6	4.8	2.8	2.9	2.4	2.5	2.5	2.0	2.8
7	5.2	2.6	2.6	2.1	2.3	2.9	1.8	2.5
8	5.9	2.4	2.4	1.8	2.0	2.3	1.5	2.3
9	6.2	2.1	2.1	1.5	1.7	2.0	1.2	2.0
10	7.2	0.9	1.9	1.3	1.3	1.7	0.9	1.7

TABLE III

Buffer: Sodium acetate-HCl.

Groundnut oil=1 c.c. F.F.A.=0.05 c.c. Sap. value=188.6. I. V.=100.1.

Difference in c.c. of $N/10$ -NaOH between the sample and the blank in case of								
Set. No.	$p_H$	Castor.	G. nut.	Seasame.	Mysore.	Safflower.	Mustard.	Cottonseed.
1	2.7	3.2	4.8	4.2	2.6	2.4	3.9	2.7
2	3.3	4.3	5.2	4.9	3.2	2.9	4.2	3.1
3	3.9	6.3	5.8	4.6	3.8	3.2	5.3	3.6
4	4.4	5.8	6.1	4.1	4.3	3.4	5.1	3.2
5	4.8	4.9	5.9	3.8	5.2	4.2	7.8	2.9
6	5.2	4.2	5.2	3.3	4.9	5.2	4.5	2.6
7	5.6	3.9	4.8	3.0	4.2	4.8	4.3	2.4
8	6.2	3.6	4.5	2.6	3.1	4.3	4.0	2.1

TABLE IV

Buffer: Sodium acetate-acetic acid.

Groundnut oil = 1 c.c.

Difference in c.c. of  $N/10$ -NaOH between the sample and the blank in case of

Set. No.	$p_H$	Castor.	G. nut.	Seasame	Mysore.	Safflower.	Mustard	Cottonseed
1	2.7	4.8	6.3	4.2	5.1	3.1	4.0	2.9
2	3.3	6.9	6.8	4.9	5.4	3.9	4.3	3.3
3	3.9	8.3	7.2	5.2	5.8	4.3	5.8	3.8
4	4.4	7.5	7.8	4.8	6.1	4.7	5.2	3.5
5	4.8	7.1	7.5	4.2	5.7	5.2	4.8	3.2
6	5.2	6.7	7.1	3.9	5.2	5.6	4.3	3.0
7	5.6	6.4	6.7	3.3	4.9	5.1	4.0	2.8
8	6.2	5.9	6.2	3.0	4.6	4.7	3.7	2.2

TABLE V

		Castor oil.		Groundnut oil.		Seasame oil.		Mysore seed oil.		Safflower oil.		Mustard oil.		Cottonseed oil.	
Lipase from		Opt. $p_H$	Max. activity in c.c.	Opt. $p_H$	Max. activity in c.c.	Opt. $p_H$	Max. activity in c.c.	Opt. $p_H$	Max. activity in c.c.	Opt. $p_H$	Max. activity in c.c.	Opt. $p_H$	Max. activity in c.c.	Opt. $p_H$	Max. activity in c.c.
1	Castor	3.6	6.1	3.8	5.2	3.8	5.0	3.6	4.7	3.8	4.3	3.6	4.1	3.8	3.3
2	Groundnut	4.4	3.8	4.4	5.3	4.4	5.1	4.8	5.5	4.4	5.1	4.8	4.7	4.4	3.2
3	Seasame	4.4	3.1	3.8	4.4	3.6	4.9	3.8	4.1	3.6	3.7	3.8	3.2	3.8	2.9
4	Mysore seed	4.8	2.8	4.8	4.6	4.4	4.3	4.8	5.0	5.2	4.8	4.8	4.5	4.8	2.5
5	Safflower	5.2	3.2	5.2	4.5	5.2	4.2	5.2	4.1	5.2	5.2	4.4	3.9	5.2	2.9
6	Mustard	3.8	2.9	3.6	5.0	3.8	4.8	3.6	4.3	3.8	4.0	3.8	6.4	3.8	2.4
7	Cottonseed	3.6	2.7	3.8	3.2	3.6	3.1	3.8	2.9	3.6	2.7	3.8	2.3	3.8	3.5

TABLE VI

*Hydrolysis of groundnut oil by different lipases using different buffers.*

Set No.	Lipase.	Disodium phosphate-citric acid buffer.		Sodium acetate-hydrochloric acid buffer.		Sodium acetate-acetic acid buffer.	
		Opt. $p_H$	Max. activity	Opt. $p_H$	Max. activity.	Opt. $p_H$	Max. activity.
1	Castor	3.8	5.2 c.c.	3.9	6.3 c.c.	3.9	8.9 c.c.
2	Groundnut	4.4	5.3	4.4	6.1	4.4	7.8
3	Seasame	3.8	4.4	3.3	4.9	3.9	5.2
4	Mysore seed	4.8	4.6	4.8	5.2	4.4	6.1
5	Mustard	3.6	5.0	3.0	5.3	3.9	5.8
6	Safflower	5.2	4.5	5.2	5.4	5.2	5.6
7	Cottonseed	3.8	3.2	3.9	3.6	3.9	3.8

From the above tables, it can be seen that the groundnut and castor cake lipases are the best active lipases and groundnut oil is the best substrate in which all the lipases show appreciable activity.

In Table VI, the combined results for the optimum  $p_H$  and the maximum activity at the optimum  $p_H$  in case of different lipases using different buffers are given. The activity of the lipase appears to go on changing with the nature of the buffer, increasing in the order: disodium phosphate-citric acid, sodium acetate-hydrochloric acid and sodium acetate-acetic acid buffer. The optimum  $p_H$  also varies with the nature of the lipase as well as the nature of the substrates, but the change in the optimum  $p_H$  in case of different substrates is small. In all the cases, the optimum  $p_H$  is in the acidic side which is a notable feature. The optimum  $p_H$  is almost constant and in only a very few cases changes with the nature of the buffer.

So it can be concluded that with the cake lipases, the optimum  $p_H$  changes with the nature of the lipase, slightly with the nature of the substrate and almost constant with different buffers. Castor and groundnut cake lipases are the best active lipases, groundnut oil is the best substrate and sodium acetate-acetic acid buffer is the best buffer.

*Effect of Buffer Concentration on the Hydrolysis of Groundnut Oil by Cake Lipases*

As the castor and groundnut cake lipases were found the most active, these two were only used for the rest of the work.

The hydrolysis of groundnut oil by different cake lipases was carried out by changing the concentration of the buffer mixture and keeping the other factors constant; sodium acetate-acetic acid buffer of 4.4  $p_H$  was used. The amount of the buffer added varied from 1 to 8 c.c. Each set of the experiments consisted of groundnut oil (1 c.c.), water (5 c.c.), cake lipase (0.1 g.) and varying quantities of acetate buffer and incubated for 24 hours at 37°. Always the blank experiment was carried out. After the period of incubation, the contents of each flask were titrated against  $N/10$  sodium hydroxide similarly under conditions as stated earlier. The results are given in Table VII.

TABLE VII

Set No.	Oil.	Buffer added.	Diff. bet the sample & the blank in c.c. of $N/10$ -NaOH in case of lipase from	
			Castor.	Groundnut.
1	1.0 c.c.	1.0 c.c.	6.9	7.2
2	"	2.0	7.5	7.8
3	"	3.0	7.8	8.1
4	"	4.0	7.0	7.3
8	"	5.0	6.7	6.2
6	"	6.0	6.3	5.9
7	"	7.0	6.1	4.8
8	"	8.0	5.8	3.9

From the above table buffer concentration appears to play an important role in the enzymic hydrolysis of oil. The optimum buffer concentration is 3 c.c.

*Effect of Substrate Concentration on the Hydrolysis of Groundnut Oil by different Cake Lipases*

The hydrolysis of groundnut oil was carried out using different lipases by changing the concentration of the oil and keeping the other factors constant using the materials in the same proportions as in earlier experiments.

Acetate buffer of  $p_H$  4.4 (2 c.c.) was used and incubated for 24 hours at  $37^\circ$ . The contents were then titrated against  $N/10$  sodium hydroxide following the same procedure as described previously. The results are shown in Table VIII.

TABLE VIII

Set No.	Oil.	Diff. bet. the sample and the blank in c.c. of $N/10$ NaOH in lipase from		Set No.	Oil.	Diff. bet. the sample and the blank in c.c. of $N/10$ NaOH in lipase from	
		Castor.	Groundnut.			Castor.	Groundnut.
1	1.0 c.c.	7.5	7.8	5	5.0	7.2	5.4
2	2.0	8.3	6.3	6	6.0	7.0	5.1
3	3.0	7.9	6.0	7	7.0	6.7	4.8
4	4.0	7.5	5.8	8	8.0	6.3	4.3

From the above table it can be seen that in general the maximum hydrolysis is obtained when substrate concentration is 1 to 2 c.c. depending on the nature of the lipase and it is very difficult if the concentration is more. Therefore the optimum substrate concentration is 1 to 2 c.c. depending upon the nature of the lipase.

*Effect of Enzyme Concentration on the Hydrolysis of Groundnut Oil by different Cake Lipases*

Eight sets of experiments were carried out keeping all other factors constant excepting the concentration of the lipase. The materials were in the same amount as used in the previous sets of experiments with varying quantities of enzyme lipase and incubated at  $37^\circ$  for 24 hours. After the period of incubation, the contents were titrated against  $N/10$  sodium hydroxide under conditions similar to previous sets of experiments. The results are given in Table IX.

TABLE IX

Set No.	Oil	Enzyme	Diff. bet the sample and the blank in c.c. of $N/10$ NaOH in lipase from		Set No	Oil	Enzyme.	Diff. bet the sample and the blank in c.c. of $N/10$ NaOH in lipase from	
			Castor	Groundnut.				Castor.	Groundnut.
1	1.0 c.c.	0.1 g.	7.5	7.8	5	1.0 c.c.	0.5 g.	8.7	8.6
2	"	0.2	7.8	8.0	6	"	0.6	9.0	8.9
3	"	0.3	8.1	8.2	7	"	0.7	9.3	9.1
4	"	0.4	8.5	8.4	8	"	0.8	9.5	9.3

The percentage hydrolysis of the oil from Table IX appears to go on increasing as the concentration of the enzyme increases. Hence, greater the concentration of the enzyme, greater is its activity.

*Effect of Temperature on Enzymic Hydrolysis of Groundnut Oil by different Cake Lipases*

Different sets of experiments were carried out by keeping the contents in the incubator at different temperatures for a fixed time and then titrating the contents against  $N/10$  sodium hydroxide. Hydrolysis of groundnut oil was carried out by keeping the contents for two hours at temperatures  $28^{\circ}$ ,  $30^{\circ}$ ,  $35^{\circ}$ ,  $40^{\circ}$ ,  $75^{\circ}$  and  $100^{\circ}$ . Experiments were conducted using the materials in the same amounts and under conditions similar to previous experiments and same procedure was followed in titrations against  $N/10$ -NaOH. The results are given in Table X.

TABLE X

Set No.	Temp.	Diff. bet. the sample and the blank in c.c. of $N/10$ -NaOH in		Set No.	Temp.	Diff. bet. the sample and the blank in c.c. of $N/10$ -NaOH in	
		Castor lipase.	Groundnut lipase.			Castor lipase.	Groundnut lipase.
1	$28.0^{\circ}$	2.7	2.5	5	$40.0^{\circ}$	3.6	3.8
2	$30.0^{\circ}$	3.2	3.0	6	$75.0^{\circ}$	2.0	2.9
3	$35.0^{\circ}$	3.5	3.3	7	$100.0^{\circ}$	0.0	0.0
4	$37.0^{\circ}$	3.7	3.6				

From Table X, it can be seen that the temperature also plays an important role in enzymic hydrolysis of the oils and that the optimum temperature for maximum hydrolysis is  $37^{\circ}$  to  $40^{\circ}$  depending on the nature of lipase.

*Effect of Salts on Enzymic Hydrolysis of Groundnut Oil by different Cake Lipases*

The cake lipases are poor in activity even though they are cheap. If they are to be utilised with advantage, they should be accelerated by using cheap accelerators. Hence the action of the following substances was studied on the hydrolysis of groundnut oil by the cake lipases with a view to ascertaining how far they accelerate the activity of the cake lipases: Strychnine sulphate, albumin, ascorbic acid, sodium taurocholate, sodium acetate, strychnine chloride, glycine, citric acid, gum arabic, acetic acid, ammonium phosphate, sodium phosphate, potassium phosphate, hydrochloric acid, calcium chloride, sodium chloride and manganese sulphate.

Each set of the experiments consisted of 1 c.c. of groundnut oil, 5 c.c. of water, 2 c.c. of acetate buffer of  $p_H$  4.4, 0.1 g. of cake lipase and 0.1 g. of salt (or 1 c.c. of  $N/10$  salt solution in case of hydrochloric acid and acetic acid), and incubated at  $37^{\circ}$  for 24 hours. Subsequent procedure followed was the same as in previous experiments. The difference between the sample and the blank in terms of c.c. of  $N/10$  sodium hydroxide will give the activity of the lipase.

The difference shows whether a particular substance is an accelerator or inhibitor depending upon whether the difference is a positive one (showing the accelerating effect) or a negative one (showing the inhibiting or retarding effect). The results are given in Table XI.

TABLE XI

Set No.	Name of the salt.	Diff in c.c. of N/10-NaOH bet the sample & the blank in		Set No.	Name of the salt	Diff in c.c. of N/10-NaOH bet the sample & the blank in	
		Castor lipase.	Groundnut lipase.			Castor lipase.	Groundnut lipase.
1	Strychnine sulphate	+0.2	-0.3	10	Gum arabic	+1.3	+0.5
2	„ chloride	+0.2	-1.2	11	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	+2.8	+1.0
3	Albumin	-0.3	-0.5	12	Na <sub>2</sub> HPO <sub>4</sub>	+1.8	+0.0
4	Sodium taurocholate	+0.5	+0.7	13	KH <sub>2</sub> PO <sub>4</sub>	+0.8	+0.3
5	Ascorbic acid	+1.0	+0.5	14	MnSO <sub>4</sub>	+0.9	+1.2
6	Sodium acetate	+0.2	+0.0	15	NaCl	+0.2	+0.4
7	Citric acid	+0.1	+0.1	16	HCl	+0.8	+1.1
8	Acetic acid	+0.8	+0.4	17	CaCl <sub>2</sub>	+0.5	+0.3
9	Glycine	+2.8	+1.8				

From the above table it appears that in general ascorbic acid, gum arabic, glycine, etc. accelerate the lipase action. In case of inorganic salts, ammonium phosphate, MnSO<sub>4</sub> and HCl are good accelerators. The organic salts accelerate more which may be due to their way of possessing N<sub>2</sub> in them. Gum arabic and ascorbic acid accelerate perhaps due to their emulsifying action.

It can be seen that the salts which are used for preparing buffer solutions do not hinder the activity of the cake lipases.

Finally it is observed that sometimes the salts which accelerate in one case may retard in another case. Hence, it will be interesting to study further this aspect as it may yield interesting results.

#### *Effect of Ageing on the Activity of Cake Lipases*

Finally it is thought that it will be better to study the effect of ageing on the activity of the cake lipase as in case this lipase is to be used on a large scale in industry, it must be very stable in its activity, at least for an appreciable amount of time. So the effect of ageing on groundnut cake lipase was studied.

Three samples of cake lipase were prepared by draining for 3 hours, one with low boiling petroleum ether, the other with acetone, the third with the mixture of acetone and low boiling petroleum ether (b. p. 56°) according to Longnecker's method (*loc. cit.*). All the three samples were completely dried, powdered and sieved through a 60 mesh sieve and used for the experiments. The hydrolysis of groundnut oil was carried out using each sample of the lipase at different period.

Each set of the experiments consisted of groundnut oil (1 c. c.), water (5 c. c.), acetate buffer (2 c. c.) of  $p_H$  4.4 and 0.1 g. of lipase of each variety at different intervals of time, kept in the incubator at  $37^\circ$  for 2 hours and then the contents titrated against  $N/10$  sodium hydroxide after the addition of 25 c. c. of neutral alcohol and warming for sometime. Always a blank accompanied the sample. The difference between the sample and the blank in terms of c. c. of  $N/10$ -NaOH gives the activity of the lipase. The results are shown in Table XII.

TABLE XII

Difference in c.c. of  $N/10$ -NaOH between the sample and the blank for groundnut lipase dried in

Set No.	Time of ageing.	Petroleum ether.	Acetone.	Pet. ether-acetone mixture.
1	0 min.	2.5	1.1	1.8
2	40	3.3	1.4	1.9
3	24 hrs.	3.6	1.5	2.1
4	2 days	3.8	1.7	2.5
5	4	4.2	1.7	2.7
6	6	4.0	1.7	2.5
7	8	3.8	1.6	2.5
8	12	3.5	1.6	2.5
9	15	3.3	1.6	2.4
10	23	3.1	1.6	2.4
11	45	2.9	1.6	2.4
12	55	2.5	1.5	2.3
13	65	2.2	1.5	2.3
14	75	2.0	1.5	2.3
15	85	1.8	1.5	2.0
16	95	1.5	1.5	2.0
17	105	1.3	1.5	1.8
18	115	1.0	1.4	1.8
19	125	0.5	1.4	1.7

It is found that in all cases the activity increases up to 2 to 4 days and then decreases. The activity is greatest in the case of petroleum ether sample, slightly less in petroleum ether-acetone mixture dried sample, and the least in acetone-dried sample. But at the same time, the velocity of change in activity is less in case of acetone-dried sample, more in petroleum ether-acetone-dried mixture, and the most in petroleum ether dried sample. In other words, the greater the activity of the sample, the more rapid is the change of activity on ageing.

Of the three samples, acetone-dried sample is the best even though its activity is low, since it keeps its activity fairly constant for an appreciable time. But acetone and petroleum ether mixture dried sample can be used for short period experiments



since its activity is appreciably good and it also keeps its activity fairly constant for a short time.

From the above observations, it can be seen that in general, the cake lipases are less active since most of their activity might have been lost in the process of removing oil from seeds due to a large amount of heat and pressure. In case there is no other cheap source of lipase available, and if the urgent necessity arises, then the castor and groundnut cake lipases obtained by ghani method can be used for enzymic hydrolysis and the best substrate and buffer are groundnut oil and sodium acetate-acetic acid buffer respectively.

DEPARTMENT OF BIOCHEMISTRY,  
INDIAN INSTITUTE OF SCIENCE,  
BANGALORE

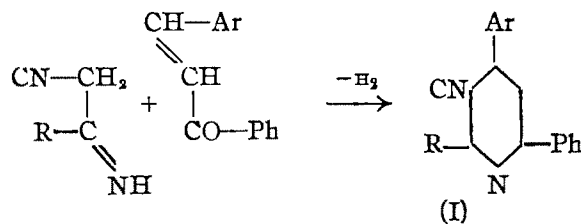
*Received May 15, 1950.*

# MEYER'S 2-METHYL-4:6-DIPHENYLPYRIDINE : DETERMINATION OF THE STRUCTURE IN VIEW OF GASTALDI'S OBJECTIONS

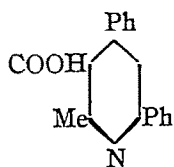
BY N. PALIT AND J. N. CHATTERJEA

The controversy regarding the constitution of Meyer's pyridines obtained from dinitriles and arylidene-acetophenones has now been solved. Gastaldi's contention about the inaccuracy of the structure of one of Meyer's pyridines as 2-methyl-4:6-diphenylpyridine is proved to be true by two other independent syntheses of the pyridine, in each case the product agreeing with Gastaldi's compound. Meyer's product is shown to be an azafluorenone formed as a by-product by a secondary reaction, the main product being the normal Gastaldi's pyridine, obviously missed by Meyer due to its greater solubility in common solvents.

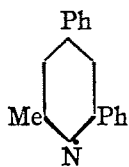
A method for the synthesis of pyridines from dinitriles was devised by V. Meyer (Meyer and Irmscher, *J. prakt. Chem.*, 1908, 78, 497). The dinitrile is condensed with an arylidene-acetophenone in the presence of sodium ethoxide :



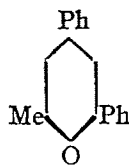
Gastaldi has thrown considerable doubt on the constitution of these products as he prepared 2-methyl-4:6-diphenylpyridine (III) (m.p. 73°) from the corresponding pyrylium salt (IV) and found it to be different from Meyer's pyridine (m.p. 156°) obtained from (I ; R=Me, Ar=Ph) by hydrolysis to (II) followed by decarboxylation (*Gazzetta*, 1922, 52, 169).



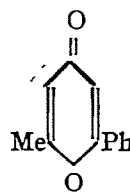
(II)



(III)



(IV)  
FeCl<sub>4</sub>



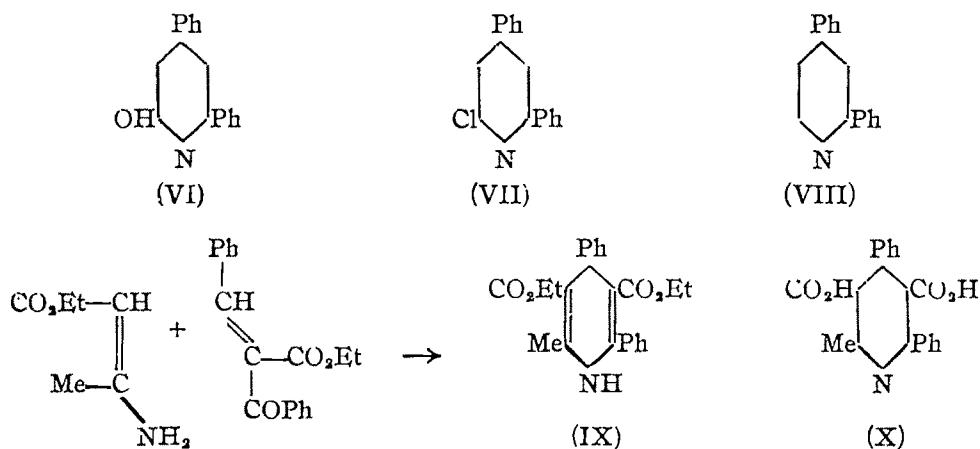
(V)

In an earlier communication by one of us, it has been shown that the structure of Meyer's compounds as a class is not incorrect and so far as the particular member, e.g. 2-methyl-4:6-diphenylpyridine is concerned, Gastaldi's contention is probably correct (Palit, this *Journal*, 1950, 27, 71).

Having established the correctness of Meyer's method, that for Gastaldi was therefore taken up. The correctness of constitution (IV) for Gastaldi's pyrylium salt received support from the work of Le Fèvre and Pearson, who synthesised the salt from benzoylacetone and acetophenone in the presence of ferric chloride and hydrochloric acid (*J. Chem. Soc.*, 1933, 1197). A convincing synthesis has now been

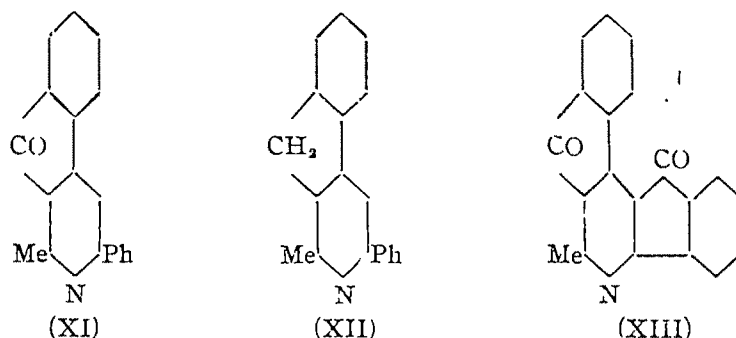
achieved by preparing the same salt from 2-methyl-6-phenyl- $\gamma$ -pyrone (V) and phenylmagnesium bromide and treating the resulting compound with ferric chloride and hydrochloric acid.

These experiments have proved conclusively that both the above routes lead to the same pyridine of unquestionable structure, and if there is any difference in (III), obtained by the two methods, the explanation must be sought in the particular compound itself. An unambiguous synthesis of (III) was therefore undertaken. For this purpose, 2-hydroxy-4:6-diphenylpyridine (VI) (Basu, this *Journal*, 1930, 7, 490) was converted into the chloropyridine (VII), but attempts to replace the halogen atom by a methyl group through the malonyl derivative proved unsuccessful (cf. Königs and Fulde, *Ber.*, 1927, 60, 2106). The catalytic reduction of (VII) with Raney nickel furnished 2:4-diphenylpyridine (VIII), but attempts to add lithiummethyl to the azomethine linkage of this compound were also abortive (cf. Zeigler and Zeiser, *Ber.*, 1930, 63, 1847). Finally, ethyl 2-aminocrotonate was condensed with benzylidene ethylbenzoylacetate in the presence of diethylamine to give the dihydropyridine (IX), which was oxidised with nitrous fumes, hydrolysed with alcoholic potash and then distilled with lime, when (III) (m.p. 73°) was exclusively obtained.



It was abundantly clear that there must be something unusual in Meyer's mode of obtaining (III) and to examine this method more critically, Meyer's experiment was repeated with due care when it was noticed that the carboxypyridine (II) underwent decarboxylation smoothly, when heated above its melting point, and the product was identical with Gastaldi's pyridine as shown by mixed m.p. and comparison of ultraviolet absorption spectrum (Fig. 1). Meyer's method of decarboxylation by soda lime, however, gave a mixture, the main product being identical with Gastaldi's pyridine. The other product, obtained in poor yield, agreed with Meyer's compound of m.p. 156°. It is the latter which crystallises more readily from solvents such as light petroleum or benzene and the main product remains in solution which is probably the cause why Meyer had missed it. This yellow product analysed as C<sub>15</sub>H<sub>13</sub>ON (Meyer gives no analysis for carbon and hydrogen) and was ketonic in character. The formation of this ketone from the acid (II) by loss of a molecule of water suggested it

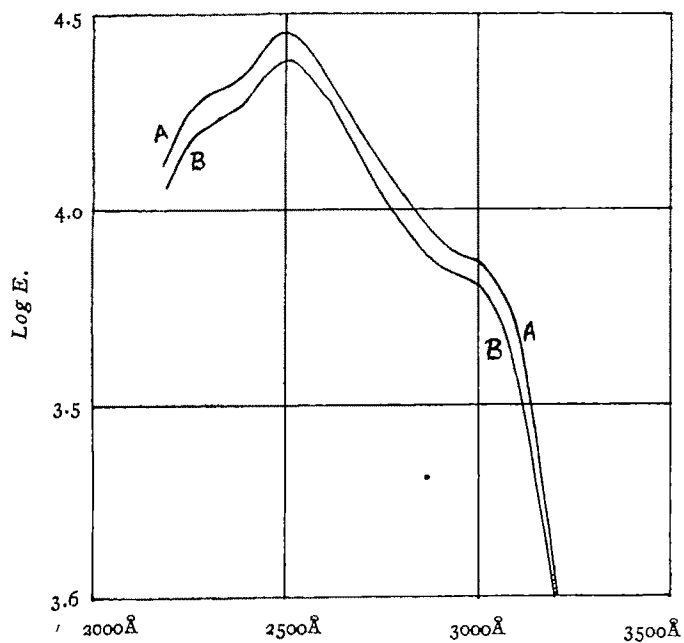
to be an azafluorenone (XI) which was confirmed by a ring-closure in the acid by concentrated sulphuric acid at 100° (cf. Mills *et al.*, *J. Chem. Soc.*, 1924, 2365) or through the corresponding acid chloride by Friedel-Crafts reaction (cf. Borsche and Hahn, *Annalen*, 1939, 537, 219). It is remarkable that the carboxy group of the acid (II) which



is so easily knocked off by mere heating above its m.p., should give the azafluorenone

Fig. 1

Absorption spectra of 2-methyl-4: 6-diphenylpyridine.



A. From Meyer's method. B. Gastaldi's compound.

even in presence of soda lime.

Reduction of (XI) by hydrazine hydrate at 200°-210° gave a quantitative yield of the azafluorene (XII) (cf. Borsche and Sinn, *Annalen*, 1937, 532, 146). The dicarboxy acid (X) on double cyclisation through the acid chloride gave 2:3:4:5-dibenzoylene-6-methylpyridine (XIII). The preparation of this diketone by an independent route has been recently described (cf. Petrow, *J. Chem. Soc.*, 1949, 2137).

#### EXPERIMENTAL

**2-Methyl-4:6-diphenylpyrylium Ferrichloride (IV).**—To a cooled solution of phenylmagnesium bromide from bromobenzene (2.5 g.) and magnesium (0.5 g.) in ether (40 c.c.) was added a solution of 2-methyl-6-phenyl- $\gamma$ -pyrone (V) (2.7 g., Ruhemann, *J. Chem. Soc.*, 1902, 93, 433). The yellowish white precipitate that appeared turned dark very soon and then the mixture was refluxed on the water-bath for 10 minutes. The complex was then decomposed with ice and hydrochloric acid. The aqueous layer was separated, treated with a solution of concentrated hydrochloric acid and ferric chloride, and the yellowish precipitate of the pyrylium salt (1.5 g.) crystallised from a

mixture of acetic anhydride and acetic acid. Compound (IV) was obtained in long yellow needles, m.p.  $172-73^{\circ}$ , undepressed on admixture with an authentic specimen prepared according to Gastaldi (*loc. cit.*). (Found. Cl, 31.6.  $C_{18}H_{18}OCl_4Fe$  requires Cl, 31.9 per cent). The salt on treatment with ammonia gave (III), m.p. and mixed m.p.,  $73^{\circ}$ .

*2-Chloro-4:6-diphenylpyridine* (VII).—A mixture of 2-hydroxy-4:6-diphenylpyridine (VI, 4.0 g.) and phosphorus oxychloride (15.0 g.) was treated with phosphorus pentachloride (15.0 g.). The mixture was heated on an oil-bath at  $165^{\circ}-170^{\circ}$  for 6 hours, decomposed with ice and extracted with ether. The ethereal solution was washed with sodium hydroxide (6%), dried with anhydrous potassium carbonate and distilled. The distillate (2.1 g.) solidified quickly (b.p.  $170^{\circ}-175^{\circ}$  / 0.24 mm.) and crystallised from petroleum ether (b.p.  $60^{\circ}-80^{\circ}$ ) in colorless prisms, m.p.  $64-65^{\circ}$ . (Found: C, 76.4; H, 4.6; N, 5.3.  $C_{17}H_{12}NCl$  requires C, 76.8; H, 4.5; N, 5.3 per cent).

*Diphenylpyridine* (VIII).—A solution of the above chloropyridine (VII, 1.0 g.) in alcoholic sodium ethoxide (sodium, 0.8 g. and dry alcohol, 50 c.c.) was hydrogenated at atmospheric pressure in the presence of Raney nickel (2 c.c., sediment). In 45 minutes the absorption of hydrogen was complete. The mixture was filtered, alcohol removed in a current of steam, the residue extracted with ether, dried (sodium sulphate) and distilled. The compound (VIII) (0.77 g.) was obtained at  $160^{\circ}-163^{\circ}$  / 0.2 mm. On cooling a solution of the distillate in petroleum ether with a sludge of dry ice in alcohol, the pyridine was obtained in prisms, m.p.  $37-39^{\circ}$ . On keeping the stable modification, m.p.  $69^{\circ}$  was obtained (Gastaldi, m.p.  $69^{\circ}$ ). (Found: C, 88.4; H, 5.8; N, 5.6.  $C_{17}H_{13}N$  requires C, 88.3; H, 5.6; N, 5.6 per cent).

The *acid sulphate* separated from dilute sulphuric acid (20%) in colorless long needles, m.p.  $250-52^{\circ}$  with slight browning (Gastaldi, m.p.  $245^{\circ}$ ). (Found: C, 62.1; H, 4.5; N, 4.1.  $C_{17}H_{13}N.H_2SO_4$  requires C, 62.0; H, 4.6; N, 4.3 per cent).

The *picrate* crystallised from alcohol in light yellow plates, m.p.  $187-88^{\circ}$  (Gastaldi, *Gazzetta*, 1922, 82, 305, gives m.p.  $187^{\circ}$ ). (Found: C, 60.3; H, 3.7; N, 11.6.  $C_{17}H_{13}N.C_6H_3O_7N_3$  requires C, 60.0; H, 3.5; N, 12.1 per cent).

The *picrolonate* was obtained from amyl alcohol in fine yellow needles, m.p.  $183-84^{\circ}$  (decomp.). (Found: C, 65.4; H, 4.4; N, 14.1.  $C_{17}H_{13}N.C_{10}H_8O_6N_4$  requires C, 65.4; H, 4.2; N, 14.1 per cent.)

*2:4-Diphenyl-3:5-dicarboethoxy-6-methyldihydropyridine* (IX).—A solution of benzylidene ethylbenzoylacetate (20.0 g.) and ethyl 2-aminocrotonate (20.0 g., used in excess) in absolute alcohol (20 c.c.) was treated with diethylamine (2.0 c.c.). The solution maintained at  $50^{\circ}$  turned yellow and the crystals of (IX) appeared in the course of 3 hours. After allowing to stand for 3 days at  $50^{\circ}-60^{\circ}$ , the crystals (16.0 g.) were collected and were obtained from alcohol in colorless needles, m.p.  $190-92^{\circ}$ . A slow evolution of gas occurs at a few degrees above the m.p.; this is probably due to the removal of a carboethoxy group followed by the aromatisation of the pyridine ring (cf. Guareschi and Grande, *Chem. Zentr.*, 1899, II, 440). (Found: N, 3.5.  $C_{24}H_{23}O_4N$  requires N, 3.6 per cent).

*2:4-Diphenyl-3:5-dicarboxy-6-methylpyridine* (X).—Nitrous fumes were passed into a cold suspension of (IX, 10.0 g.) in alcohol (25 c.c.). The solid gradually passed into solution which was poured on ice, extracted with ether and washed with sodium

carbonate. The ethereal solution was dried (potassium carbonate) and gave on evaporation 2:4-diphenyl-3:5-dicarboethoxy-6-methylpyridine as a viscous liquid which was hydrolysed with alcoholic potash (50 c.c., 30%) by boiling under reflux for 5 hours. The potassium salt separated in an hour. It was collected (8.2 g.) and washed successively with a small amount of dry alcohol and dry ether. The salt is very hygroscopic. The corresponding acid (X) (3.2 g.) was obtained on treating the salt (4.0 g.) with an equivalent amount of hydrochloric acid. It crystallised from aqueous alcohol (charcoal) in colorless prismatic needles, m.p. 287-88° (decomp.). The crystals contain water of crystallisation which is easily removed by heating in vacuum at 120° for 1 hour. (Found: N, 4.4; equiv., 165.5.  $C_{20}H_{15}O_4N$  requires N, 4.2 per cent. Equiv., 166.5).

*2-Methyl-4:6-diphenylpyridine* (III).—An intimate mixture of the above potassium salt (3.5 g.) and calcium hydroxide (7.0 g.) was heated strongly in a horizontal tube closed at one end. A thick oil, which distilled slowly, solidified readily (1.4 g.) and crystallised from petroleum ether in colorless prisms, m.p. 69-70°. On purification by chromatography in petroleum ether solution on alumina (Brockmann), (III) was obtained pure, m.p. 73°, undepressed on admixture with Gastaldi's pyridine. (Found: N, 5.7.  $C_{18}H_{15}N$  requires N, 5.7 per cent).

*Decarboxylation of Meyer's Acid* (II). *Method (a)*.—The acid was heated on a metal bath the temperature of which was gradually raised from 260° to 290°. The evolution of carbon dioxide was complete in a few minutes. The residue on distillation gave a quantitative yield of (III), which on purification by chromatography, was obtained in prisms, m.p. 73°, undepressed on admixture with Gastaldi's pyridine. (Found: C, 88.1; H, 5.9; N, 5.6.  $C_{18}H_{15}N$  requires C, 88.1; H, 6.1; N, 5.7 per cent).

The *picrate* crystallised from butanol in yellow plates, m.p. 213° (Dilthey, *J. prakt. Chem.*, 1916, **94**, 53, gives m.p. 212-13°). (Found: C, 61.0; H, 3.5; N, 12.0.  $C_{18}H_{15}N \cdot C_6H_3O_7N_3$  requires C, 60.8; H, 3.8; N, 11.8 per cent).

The *picrolonate* crystallised from alcohol in yellow needles, m.p. 187-88° (decomp.). (Found: C, 66.0; H, 4.4; N, 13.9.  $C_{18}H_{15}N \cdot C_{10}H_8O_6N_4$  requires C, 66.0; H, 4.4; N, 13.8 per cent).

*Method (b) (Meyer's method)*.—An intimate mixture of the acid (1.0 g.) and soda lime (4.0 g.) was heated carefully with a smoky flame in vacuum and the distillate was collected on a cold finger. This was dissolved in petroleum ether, filtered and concentrated. The solution deposited yellow needles (ca. 50 mg.), m.p. 148-52° which were purified by chromatography in petroleum solution on an alumina column. The yellow band (green fluorescence in ultraviolet light) was eluted by a mixture of petroleum ether and benzene (3:2). The material crystallised from light petroleum in yellow leaflets, m.p. 156° (Meyer, m.p. 156°). The compound is feebly basic and dissolves in concentrated sulphuric acid with a deep yellow solution. (Found: C, 83.9; H, 5.0; N, 5.3.  $C_{10}H_{11}ON$  requires C, 84.1; H, 4.8; N, 5.2 per cent). The compound was ketonic and furnished an oxime, m.p. 290° (decomp.) which was not depressed on admixture with the oxime of (XI) mentioned below. The petroleum mother-liquor on concentration gave a gummy mass (0.5 g.) which slowly crystallised. This was identified as (III) by m.p. and mixed m.p.

*1-Methyl-3-phenyl-2-azafluorenone* (XI). *Method (a)*.—The compound (II) (1.5 g.) was converted into the acid chloride by refluxing with thionyl chloride (8 c.c.) for 4

hours. The crystalline acid chloride was dissolved in warm freshly distilled nitrobenzene (30 c.c.) and then cooled and treated with anhydrous aluminium chloride (1.7 g.) in small portions. The deep yellow coloured mixture was maintained at 50°-60° for 1½ hours. The complex was then decomposed with ice and hydrochloric acid and the nitrobenzene removed in a current of steam. The residue was treated with sodium acetate (10 g.) and the sulphur-yellow precipitate (1.3 g.) was collected and crystallised from a mixture of benzene and light petroleum. The compound (XI) was obtained in light yellow flat needles, m.p. 155-56°, undepressed on admixture with Meyer's so-called "2-methyl-4:6-diphenylpyridine". The compound dissolved in concentrated sulphuric acid giving a deep yellow solution. (Found: N, 5.2.  $C_{10}H_{13}ON$  requires N, 5.2 per cent).

*Method (b).*—The acid (II, 0.2 g.) was dissolved in concentrated sulphuric acid (1 c.c.) and heated at 100° on the water-bath for 8 hours. On pouring the orange-red solution into water, a yellow crystalline precipitate at once appeared. The whole was made alkaline to litmus and the precipitate collected (0.18 g.) and crystallised from petrolbenzene mixture in flat yellow needles, m.p. 156°.

*Oxime.*—A solution of the ketone (0.5 g.) in pyridine (25 c.c.) was heated on the steam-bath with hydroxylamine hydrochloride (0.5 g.) for 1½ hours and then left over night at the room temperature. The oxime, precipitated by addition of water, crystallised from butanol in fine, long, colorless needles (0.3 g.), m.p. 291-92° (decomp., darkening at 285°). (Found: N, 9.7.  $C_{10}H_{14}ON_2$  requires N, 9.8 per cent).

*1-Methyl-3-phenyl-2-azafluorene (XII).*—The above ketone (XI, 0.3 g.) was treated with hydrazine hydrate (1 c.c., 100%) and heated in a sealed tube at 200°-210° for 24 hours. The azafluorene was obtained as a colorless solid (0.27 g.), crystallising from methyl alcohol in light colorless needles, m.p. 104-105°. (Found: N, 5.5.  $C_{19}H_{18}N$  requires N, 5.4 per cent). The *picrate* was obtained from methyl alcohol in yellow needles, m.p. 209-11° (decomp.). (Found: N, 11.4.  $C_{19}H_{18}N.C_6H_5O_7N_3$  requires N, 11.5 per cent).

*2:3:4:5-Dibenzoylene-6-methylpyridine (XIII).*—The acid (X, 1.4 g.) was converted into the acid chloride by heating with thionyl chloride (20 c.c.) for 2 hours. A cold solution of the acid chloride in nitrobenzene (15 c.c.) was treated with anhydrous aluminium chloride (2.4 g.), the whole allowed to attain the room temperature and then warmed at 60°-65° for 11 hours. The mixture was then decomposed with ice and hydrochloric acid and nitrobenzene removed by steam distillation. A dark brown gum was left which was boiled with a mixture of ethyl alcohol (130 c.c.) and *n*-butyl alcohol (100 c.c.). The yellow crystalline precipitate (0.45 g.) after treatment with alkali was crystallised from pyridine in yellow needles. m.p. 260-62°. Petrow (*loc. cit.*) gives m.p. 263° (corr.). (Found: N, 4.7.  $C_{20}H_{11}O_2N$  requires N, 4.7 per cent). The compound gives a deep yellow coloration with concentrated sulphuric acid. The *dioxime* crystallised from pyridine in nearly colorless needles, which shrinks at 320° and decomposes at higher temperature. (Found: N, 12.6.  $C_{20}H_{13}O_2N_3$  requires N, 12.8 per cent).

The absorption spectra were taken by Dr. F. B. Strauss of Oxford. One of us (J. N. C.) thanks Prof. Sir Robert Robinson, O. M., P. R. S., for helpful discussion.

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SCIENCE COLLEGE, PATNA.

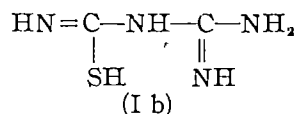
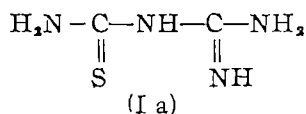
Received February 3, 1950.

## COMPLEX COMPOUNDS OF THIODICYANDIAMIDINE WITH METALLIC ELEMENTS. PART I

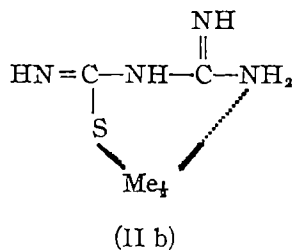
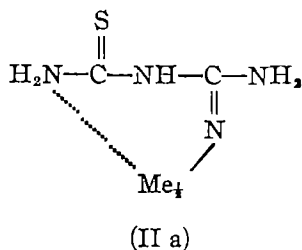
BY PRIYADARANJAN RÂY AND AJOY KUMAR CHAUDHURY

Thiodicyandiamidine (guanylthiourea) has been found to act as a bifunctional ligand yielding complexes of the inner metallic type with copper and nickel. The constitution of these complexes has been discussed.

Thiodicyandiamidine or guanylthiourea (I) has been found to act as a bifunctional ligand resembling biguanide and dicyandiamidine, yielding, with bivalent metals like copper and nickel, complex compounds of the inner metallic type (II).



It can react in either of its tautomeric forms (a) or (b) to give rise to inner metallic complexes of the structures shown below :

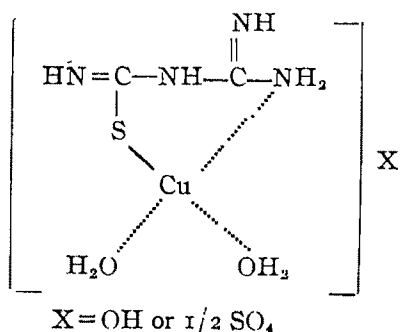


[Me = Cu or Ni]

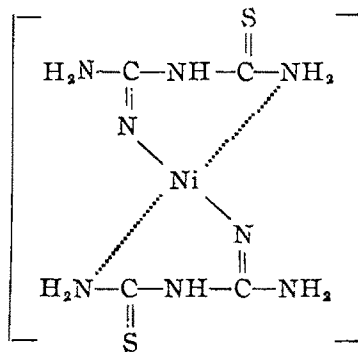
As the colour of the copper complex is brown, while that of nickel is orange, it may be assumed that the configuration of the former corresponds to the structure (II b) and that of the latter to (II a). For, it is well known that all nickel complexes of the inner metallic type, with the nickel atom linked to four N atoms in the complex, are yellow, orange or red. Typical instances of this are furnished by the ligands like biguanides and glyoximes. The brown colour of copper complex suggests strongly of the presence of a copper—sulphur bond. This is further supported by its ready decomposition into black sulphide of copper. The corresponding nickel complex, on the other hand, fails to give any nickel sulphide even with boiling alkali solutions. Then again, while nickel combines, as usual, with two molecules of thiodicyandiamidine filling up all the four co-ordination positions, copper unites with only one molecule of the ligand occupying two of its co-ordination positions, the other two being filled up by water molecules (III). This constitutes an important distinction between copper and nickel in respect of their thiodicyandiamidine complexes. But the configuration



(IV) for the nickel complex with two free amino groups would rather make it behave as a diacidic base like its biguanide analogues. But the fact that the compound is incapable of forming salts with acids may be attributed to the presence of the acidic



(III)



(IV)

thio-amido group  $\text{S}=\text{C}_1-\text{NH}_2$  in the molecule. This is also in parallel with the behaviour of nickel dicyandiamidine complex. So, while the nickel ion reacts with thiodicyandiamidine in its tautomeric form (I a), copper reacts more easily with its thiol form (I b).

Measurement of magnetic susceptibilities indicates that the copper and nickel complexes possess planar configuration with  $dsp^2$  hybrid bonds.

### EXPERIMENTAL

Thiodicyandiamidine was prepared from dicyandiamide and sulphuretted hydrogen according to the method described by Bamberger (*Ber.*, 1883, **16**, 1460). Oxalate of the base was prepared from the product of the reaction by treatment with ammonium oxalate and oxalic acid, and purified by recrystallisation. (Found: N, 31.63; S, 17.90; oxalic acid, 34.06.  $2\text{C}_2\text{H}_6\text{N}_4\text{S} \cdot \text{C}_2\text{H}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  requires N, 31.0; S, 17.60; oxalic acid, 34.80 per cent).

From the oxalate, pure base was obtained by treatment with baryta solution; m. p. of the base,  $160^\circ$ . (Found N, 47.10; S, 26.90.  $\text{C}_2\text{H}_6\text{N}_4\text{S}$  requires N, 47.45; S, 27.10 per cent).

*Cupric monothiodicyandiamidine sulphate* was obtained as a brown precipitate when a solution of copper sulphate (1.25 g.) was added to that of thiodicyandiamidine (1.18 g.). The product was filtered, washed with cold water, and then dried in air. The substance is insoluble in cold water, but slightly soluble in hot water; the solution yields a white precipitate of  $\text{BaSO}_4$  with barium chloride. On warming with dilute acid or alkali solution it gives a black precipitate of copper sulphide. On heating to  $105^\circ$  it blackens due to the formation of copper sulphide. {Found: Cu, 21.06; N, 18.43; S (total), 15.82;  $\text{SO}_4$ , 15.78;  $\text{H}_2\text{O}$  (by loss at  $100^\circ$ ), 11.66.  $[\text{Cu}(\text{C}_2\text{H}_6\text{N}_4\text{S})(\text{H}_2\text{O})_2]_2 \cdot \text{SO}_4 \cdot 4\text{H}_2\text{O}$  requires Cu, 21.13; N, 18.63; S (total), 15.97;  $\text{SO}_4$ , 15.96;  $\text{H}_2\text{O}$  (4 mol.), 11.96 per cent}.

The substance (dried at  $100^\circ$ ) gives Cu, 23.90 ; S(total), 18.20 ;  $[\text{Cu}(\text{C}_2\text{H}_5\text{N}_4\text{S})(\text{H}_2\text{O})_2]_2 \text{SO}_4$  requires Cu, 24.01 ; S(total), 18.14 per cent.

*Cupric monothiodicyandiamidine hydroxide* was obtained from a cold solution of copper sulphate (1.25 g) and that of thiodicyandiamidine (1.18 g.) in the presence of an excess of ammonium hydroxide. The product was filtered, washed with cold water, and then dried in a desiccator to a constant weight.

The substance forms brown crystals, insoluble in water and alcohol. It liberates ammonia from solutions of ammonium salts. It is decomposed by warm dilute hydrochloric acid with separation of black sulphide of copper. When heated to  $100^\circ$  it blackens due to the formation of CuS. {Found: Cu, 27.38 ; N, 24.12 ; S, 13.64.  $[\text{Cu}(\text{C}_2\text{H}_5\text{N}_4\text{S})(\text{H}_2\text{O})_2] \text{OH}$  requires Cu, 27.19 ; N, 23.98 ; S, 13.70 per cent}.

*Nickel tris-thiodicyandiamidine* was prepared by the addition of a solution of nickel sulphate (1.4 g.) to that of thiodicyandiamidine (1.18 g.) in the presence of a large excess of caustic soda. The orange coloured precipitate was filtered, washed with cold water and dried in a desiccator to a constant weight. The substance is insoluble in water and alcohol. It liberates ammonia from ammonium salts, but is unaffected by boiling caustic soda solution. It is readily decomposed by warm dilute acids. {Found: Ni, 18.40 ; N, 34.91 ; S, 19.90 ;  $\text{H}_2\text{O}$  (by loss at  $100^\circ$ ), 8.40.  $[\text{Ni}(\text{C}_2\text{H}_5\text{N}_4\text{S})_3] \cdot 1.5 \text{H}_2\text{O}$  requires Ni, 18.35 ; N, 35.03 ; S, 20.01 ;  $\text{H}_2\text{O}$ , 8.40 per cent}.

{Found (for the anhydrous substance): Ni, 20.09 ; N, 38.06 ; S, 21.90. Calc. Ni, 20.05 ; N, 38.26 ; S, 21.86 per cent}.

*Magnetic Susceptibilities.*—The magnetic susceptibilities of the compounds were measured in a Gouy's balance. The results are given below.

Substance	$\chi_g$	$\chi_M(\text{obs.})$	$\delta(\text{diamagnetic correction})$	$\chi_M(\text{corr.})$	$\mu_B$
1. $[\text{Cu}(\text{C}_2\text{H}_5\text{N}_4\text{S})(\text{H}_2\text{O})_2]_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$	$2.70 \times 10^{-6}$	$1623 \times 10^{-6}$	$207 \times 10^{-8}$	$1830 \times 10^{-6}$	1.50
2. $[\text{Cu}(\text{C}_2\text{H}_5\text{N}_4\text{S})(\text{H}_2\text{O})_2]\text{OH}$	$3.45 \times 10^{-6}$	$805.5 \times 10^{-6}$	$65.6 \times 10^{-8}$	$871 \times 10^{-6}$	1.46
3. $[\text{Ni}(\text{C}_2\text{H}_5\text{N}_4\text{S})_3] \cdot 1.5\text{H}_2\text{O}$	Diamagnetic				

The moment values for the copper atom in the copper complexes are somewhat lower than the theoretical value of  $1.73 \mu_B$ , which suggests an unusually high temperature effect.

## QUINOLINE DERIVATIVES. PART XV

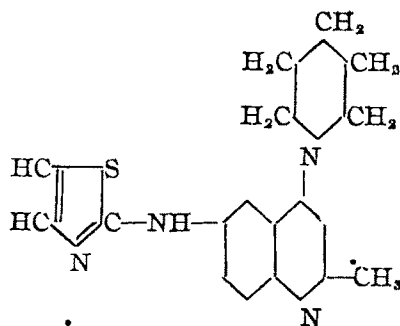
By T. N. GHOSH

Synthesis of a thiazylaminoquinoline derivative containing a piperidino group is described.

In recent years certain quinoline and *isoquinoline* derivatives (Kreitman, *Arch. Exp. Path. Pharm.*, 1932, **164**, 509; Ellinger *et al.*, *Klin Woch*, 1934, **13**, 411; German Patent, 549,967) have been found to possess antispasmodic activity. Of the former, reference is made to the synthesis of some pyridylquinolines and thiazylquinolines (Heilbron and co-workers, *J. Chem. Soc.*, 1943, 401), some of which have shown some promise as spasmolytic agents. That the presence of sulphur-containing groups like thiazyl, thienyl, etc., may promote such activity is indicated by the recent observations (Blicke and Tsao, *J. Amer. Chem. Soc.*, 1944, **66**, 1645; Adamson and Green, *Nature*, 1950, **165**, 122) about the pronounced spasmolytic activity of certain thiophene derivatives containing tertiary bases.

From a general survey of the chemistry of antispasmodics (cf. Blicke *et al.*, *J. Amer. Chem. Soc.*, 1939, **61**, 93, 771, 774) it is found that they are, in general, salts of secondary or tertiary bases. It has been therefore considered to be of interest to synthesise quinoline derivatives containing both the thiazylamino group and tertiary bases and to see if antispasmodic activity might be found in such a class of compounds.

2-Methyl-4-hydroxy-6-aminoquinoline (Jacini, *Gazzetta*, 1939, **69**, 111; Kermack and Weatherhead, *J. Chem. Soc.*, 1939, 563) has now been converted into the corresponding 6-thiocarbamido derivative (I), which, when reacted with  $\alpha\beta$ -dichlorodiethyl ether, has easily furnished the corresponding 6-(thiazyl-2'-)amino derivative (II). When treated with phosphorus oxychloride, the compound (II) has yielded the corresponding 4-chloro derivative (III). The condensation of (III) with piperidine results in the formation of the corresponding 4-piperidino derivative (IV) (cf. Kermack and Weatherhead, *loc. cit.*), the pharmacological examination of which is in progress.



(IV)

Compounds other than ketones, but containing an active methyl or methylene group, may sometimes be induced to respond to the Mannich reaction (cf. Kermack and Muir, *J. Chem. Soc.*, 1931, 3089; Pathak and Ghosh, this *Journal*, 1949, **26**, 371). In fact, Kermack and Muir (*loc. cit.*) have shown that the methyl group in quinaldine reacts with formaldehyde and secondary amines to give rise to tertiary bases. In order to introduce another tertiary base into (IV), the condensation of (IV) with formaldehyde and a secondary amine was attempted under a variety of conditions but without success.

#### EXPERIMENTAL

*2-Methyl-4-hydroxy-6-thiocarbamidoquinoline* (I).—To an aqueous solution of 2-methyl-4-hydroxy-6-aminoquinoline hydrochloride (12 g., Jacini, *loc. cit.*) potassium thiocyanate (10 g.) was added. The solution was heated on the water-bath to dryness and the solid treated with water. The mixture was again evaporated to dryness. This operation was repeated once more and the solid finally baked on the water-bath for 1 hour. The solid was finely powdered, triturated with cold dilute hydrochloric acid, filtered and thoroughly washed with water. It is insoluble in boiling water and in almost all organic solvents, and could not therefore be further crystallised. It was therefore washed thoroughly with hot alcohol and ether and obtained as a yellowish granular solid (11 g.) which decomposes at 270°-272°, with evolution of gas, to a brown pasty solid. (Found: N, 17.71.  $C_{11}H_{11}ON_3S$  requires N, 18.02 per cent).

It is insoluble in cold dilute hydrochloric acid but readily soluble in cold dilute alkali. It is rather unstable even towards cold dilute alkali, the conversion into 6-amino-compound taking place within a short time.

*2-Methyl-4-hydroxy-6 (thiazyl-2'-) aminoquinoline* (II).—The above compound (I, 10 g.) was thoroughly triturated with water (100 c.c.) and while the mixture was heated under reflux on the water-bath,  $\alpha\beta$ -dichlorodiethyl ether (10 g.) was gradually added under shaking. On heating and shaking a clear solution was gradually obtained which was further heated on the water-bath for 2 hours. Next day the solution was diluted with water and basified with ammonium hydroxide when a brown solid was obtained. It was purified by solution in cold dilute hydrochloric acid, shaking the clear solution with ether and by basifying the aqueous solution with ammonium hydroxide. The brown granular solid (9.2 g.), thus obtained, is practically insoluble in boiling water and in most of the organic solvents. It was, however, crystallised from nitrobenzene as a brownish crystalline powder. It becomes deep chocolate coloured on heating and does not melt even at 300°. (Found: N, 16.68; S, 11.97.  $C_{13}H_{11}ON_3S$  requires N, 16.34; S, 12.45 per cent).

The compound (II) is not readily soluble in cold dilute alkali but goes into solution on standing. It is, however, readily soluble in cold dilute hydrochloric acid. In acetic acid the compound is readily soluble and is not precipitated on dilution with water, indicating the formation of a salt with acetic acid. However, the base is completely precipitated when basified with ammonium hydroxide. The solution of the compound in nitrobenzene does not desulphurise yellow oxide of mercury, indicating the presence of sulphur in the ring and the formation of the thiazole ring.

*2-Methyl-4-Chloro-6-(thiazyl-2'-)aminoquinoline* (III).—The compound (II, 12 g.) was gradually added to phosphorus oxychloride (50 c.c.), when a thick solution was obtained with rise in temperature. The solution was heated in an oil-bath under reflux at 120°-125° for 2 hours and at 125°-130° for a further period of 2 hours. Next day, the excess of phosphorus oxychloride was distilled under reduced pressure and the residue, after being cooled in ice, was treated with cold water when a dark coloured solution was obtained with rise in temperature. The solution was basified with caustic soda solution, when a solid was precipitated which, after being allowed to stand for one hour under occasional stirring, was filtered and thoroughly washed with water. It is readily soluble in alcohol, ether and other organic solvents and was crystallised from aqueous alcohol (charcoal) in yellowish rectangular plates (8 g.), m.p. 206°-207°. It was dried at 105°-110° *in vacuo*. (Found: N, 15.25.  $C_{13}H_{10}N_3ClS$  requires N, 15.25 per cent). It is readily soluble in cold, dilute mineral acids but insoluble in alkali.

*2-Methyl-4-piperidino-6-(thiazyl-2'-)aminoquinoline* (IV) —A mixture of the compound (III, 5 g.) and piperidine (7.5 c.c.) was heated on the water-bath for 4 hours. The thick, dark coloured solution was poured into water when a pasty mass was precipitated. The mixture was steam-distilled and the residue was cooled and powdered. The solid was further purified by solution in dilute hydrochloric acid and reprecipitation by ammonium hydroxide. It was finally crystallised from acetone-benzene mixture (1:1) in brown, rectangular plates (2.8 g.), m.p. 238-40°. (Found: N, 16.95.  $C_{18}H_{20}N_4S$  requires N, 17.28 per cent) It is insoluble in alkali but readily soluble in dilute mineral acids. It is soluble in most of the organic solvents but practically insoluble in boiling water.

## INVESTIGATIONS ON NICKEL AMMINES. PART II. PRECIPITATION OF NICKELOUS HYDROXIDE UNDER DIFFERENT CONDITIONS AND ITS SOLUBILITY IN AQUEOUS AMMONIA

BY C. SHUDHIR SHAW AND SATYESHWAR GHOSH

Observations on the solubility of nickelous hydroxide, prepared by using different proportions of nickel and hydroxyl ions, have been recorded. The difference in solubility of the different samples has been ascribed to the amphoteric nature of the hydroxide.

It is interesting to note that there is a wide variation in the observations of various workers regarding the solubility of hydrated nickelous oxide in aqueous ammonia solutions; workers like Bonsdroff (*Z. anorg. Chem.*, 1904, **41**, 185) and Strack (*Ber.*, 1903, **36**, 3840), while giving their observations, suggest that the variation and non-agreement in their results are due to the different modifications of the hydrated oxide employed by them. The existing literature, however, does not convey any conclusive explanation of the different modifications of nickelous hydroxide.

In our detailed study of the complex ammines of nickel (to be published later) it was considered necessary to investigate those varying conditions which lead to differences in the solubility of the nickelous hydroxide in aqueous ammonia. In this paper we have employed nickelous hydroxide prepared by using different proportions of nickelous salt and alkali, in order to elucidate the nature of the hydroxide obtained under different conditions, and its effect, on its solubility.

We have observed that nickelous hydroxide, precipitated from a soluble nickel salt by caustic soda, generally requires smaller quantities of the alkali for complete precipitation. In the cold about 12% less alkali is required than the theoretical quantity for complete removal of nickel from an  $M/2$  solution, whereas in the hot a still smaller quantity is sufficient for complete precipitation. Similar observations have been recorded by Britton (*J. Chem. Soc.*, 1925, 2210). We have, however, noted that the amount of alkali needed, approaches the theoretical value for dilute nickel salt solutions. We find that the character of the hydroxide precipitated by deficient, equivalent, and a slight excess of caustic soda, in the cold, differs remarkably in its capacity to dissolve in aqueous ammonia. The solubility was found to be the least for samples obtained with increasing quantities of alkali. A similar phenomenon has been observed by Dey and Ghosh (this *Journal*, 1947, **24**, 181) and Mehrotra and Ghosh (*Proc. Nat. Acad. Sci., India*, 1946, **16**, 161) in the case of cupric hydroxide.

### EXPERIMENTAL

Three samples, A, B and C, of nickelous hydroxide precipitates were obtained by the interaction of a fixed volume of nickel sulphate with varying amounts of caustic soda solutions, as shown in the following table.

TABLE I

150 c.c. of  $M/2$ - $\text{NiSO}_4$  solution  $\equiv$  138.7 c.c. of 1.082*N*- $\text{NaOH}$  solution.  
Temp. = 30°.

Sample	Vol. of $M/2$ - $\text{NiSO}_4$ .	Vol. of $\text{NaOH}$ .	Remarks.
A	150 c.c.	118.7 c.c.	Alkali, 14.38% less
B	150	138.7	Alkali, equivalent
C	150	158.7	Alkali, 14.38% excess

The precipitation was carried out at a room temperature of 30°, with continuous stirring. The nickelous hydroxide formed was filtered and washed with cold distilled water till the filtrate was free from nickel, alkali and sulphate ions. The precipitates were then shaken vigorously with distilled water to make a homogeneous suspension, and the final volume raised to 500 c.c. Nickel content of the suspension was then estimated volumetrically using potassium cyanide (cf. Treadwell and Hall, "Analytical Chemistry", Vol. II, p. 680), and several estimations from 10 c.c. of the suspension gave concordant results. The final volume of the three suspensions were so adjusted that the nickel content was the same in all the three cases. The sulphate in each of the finally diluted suspensions was then estimated and the following results were obtained.

TABLE II

Nickel in mg. atoms per litre = 98.65.

Sample	Sulphate in mg. $M$ ion per litre.
A	0.5059
B	0.5012
C	0.3857

The above table shows that the sulphate is associated with the precipitates and it decreases with increasing quantity of alkali employed for precipitation. These results are in agreement with those obtained by Dey and Ghosh (*loc. cit.*) in the case of cupric hydroxide.

*Solubility in Aqueous Ammonia Solutions.*—Each of the suspensions (25 c.c.) containing the same amount of nickel was taken in glass stoppered Jena glass bottles and 50 c.c. of aqueous ammonia solutions of different concentrations were added, so that the final concentration of ammonia in each was 0.5*M*, 1.0*M*, 1.5*M*, 2.0*M*, 2.5*M* and 3.0*M* respectively. The suspensions with the aqueous ammonia were allowed to stand for approximately 18 to 20 hours at room temperature (30°) with occasional shaking, when the nickel content in the solution became constant. The suspensions were then filtered through a double layer of Whatman's No. 42 filter papers, and nickel was estimated in 25 c.c. of the filtrate. The following table gives the results.

TABLE III

Nickel in each suspension = 98.65 mg. atoms per litre.

Final conc. of ammonia soln.	Amount of nickel dissolved in mg. atoms per litre of suspension		
	A.	B.	C.
0.5M	0.3312	0.2473	0.1628
1.0	2.561	2.303	2.058
1.5	4.745	4.310	3.951
2.0	7.442	6.775	6.357
2.5	12.00	11.570	10.250
3.0	14.090	17.540	11.330

The above results show that the sample of nickelous hydroxide precipitated with excess of alkali is more soluble. It is also observed that the three types of precipitates show a variation in their physical properties, namely, the size of the particles, a slight variation in colour, ranging from olive green to whitish green, and the gelatinous nature of the precipitates. Thus the precipitates obtained with excess of alkali are more compact.

It was thought necessary to see the effect of the grain size of the particles of the hydroxide on its solubility in ammonia solutions. For this purpose nickelous hydroxide sample was obtained by precipitating the hydroxide with excess of alkali (14.4% more than the equivalent amount) at 80°, and an even suspension was obtained as described above and contained no free nickel or hydroxyl ions but only a small quantity of sulphate ion associated with the precipitate. This suspension was divided in two parts, P and Q. The portion Q was then thoroughly ground in an agate mortar, small amounts at a time, the whole operation lasting for about four hours. The volume of the suspensions was then raised to 200 c.c. each. Nickel in both the suspensions was the same, namely 86.62 mg. atoms/litre. The sulphate associated in each of the finally diluted suspensions was estimated and was found to be identical. The difference in the size of the particles of the suspensions was established by taking the two suspensions in two long tubes (1 cm. diameter) and noting the time taken by the suspensions to settle down through a fixed height, as noted below.

TABLE IV

Distance settled.	Time taken by		Distance settled.	Time taken by	
	P.	Q.		P.	Q.
1 cm.	51 mins.	20 mins.	20 cm.	105 mins.	140 mins.
2	33	45	25	130	175
3	60	80	30	170	222
15	85	125			

It is thus observed that the precipitate, which was ground, takes a longer time to settle, showing the particles of the precipitate in the suspension Q are smaller in size than those of the other.

The solubilities of these two types of precipitates in 0.5M, 1.0M and 1.5M aqueous ammonia solutions were determined by the method already described. The following results were obtained.

TABLE V

Nickel in each of the suspensions = 86.62 mg. atoms per litre.

Final conc. of ammonia.	Amount of dissolved Ni in mg. atoms per lit. of NH <sub>3</sub> in suspension	
	P.	Q.
0.5 M	0.1614	0.1610
1.0	2.0530	2.0510
1.5	4.0780	4.0760

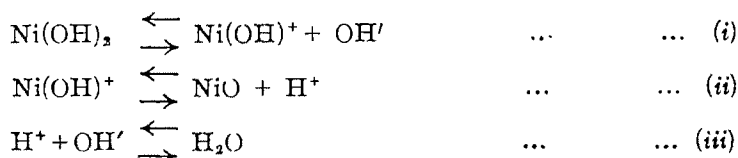
It is thus evident from the above table that reduction in the size of the particles has no remarkable effect on the solubility of the hydroxide in aqueous ammonia solution.



## DISCUSSION

From the experimental results the solubility of the hydroxide samples precipitated with excess of alkali appears to be least soluble; whereas those with deficient alkali are more soluble, and further the solubility is more related to the chemical character rather than the grain size of the precipitated hydroxide.

Considering the amphoteric nature of nickelous hydroxide, we may consider the following reactions occurring on the surface of the hydroxide:



According to the above scheme, equation (i), nickelous hydroxide behaves as a base, and in equation (ii),  $\text{H}^+$  ion is liberated. Naturally, if  $\text{OH}'$  ions are deficient in the system  $\text{NiSO}_4\text{--NaOH}$ , the equation (i) will proceed from left to right and thus anions like sulphate will be preferentially associated by the precipitate because of its basic character. If, however,  $\text{OH}'$  ions are in excess in the system, the equation (ii) will proceed from left to right and the hydroxide will show acidic properties, thus diminishing the chances of the adsorption of sulphate ions.

For the formation of ammines the necessary electrons are supplied by the ammonia molecules. Each ammonia molecule donates two electrons. If, therefore, the nickelous hydroxide is converted, of course, partially into  $\text{Ni(OH)}^+$ , the affinity for electrons will increase, and the tendency of the formation of an ammine will then be very prominent.

We are of the opinion that the solubility of nickelous hydroxide in ammonia, due to the formation of an ammine, first passes through a colloidal stage, and finally goes to complete dissolution forming complex ammino-nickel ion with increasing concentration of ammonia (cf. Dey, *J. Colloid Sci.*, 1948, **3**, 373; Ghosh and Dhar, *J. Phys. Chem.*, 1924, **28**, 457; 1926, **30**, 628). It is but apparent that an acid surface of  $\text{Ni(OH)}^+$ , as represented by equation (ii), will be a favourable condition for the adsorption of ammonia to form a colloidal solution.

The quantity of sulphate associated with the precipitate varies with the amount of alkali used for precipitation, but the formation of the nickel ammine does not seem to be directly dependent on the amount of adsorbed sulphate. Thus, in Table III, we find that the variation in the solubility of nickelous hydroxide is considerable in samples A and B, though the difference in the amount of sulphate lies within 1%.

We thus conclude that for the favourable formation of complex nickel ammines from hydrated nickelous oxide, the precipitate must be obtained with a lesser amount of alkali since excess of alkali gives a precipitate which is likely to be chemically less active and is thus unsuitable for co-ordination.

Further work on nickel ammines is in progress, which will substantiate the view advanced in this paper and will form the subject matter of subsequent communications.

## METALLIC COMPLEXES OF TARTARIC AND CITRIC ACIDS. PART II. COPPER-ALKALI TARTRATE

BY R. N. SEN SARMA

From conductometric measurements it has been shown that in dilute solution cupric ion reacts with alkali tartrate just like the free acid resulting in the formation of a complex containing metal and tartrate ion in the proportion of 1 : 1. By utilising Job's method of continued variation the instability constant of the complex has been determined. The mean value of  $K$ , the instability constant found, is  $6.1 \times 10^{-3}$ .

In a previous communication (this *Journal*, 1950, 27, 443) the results of the observations with tartaric acid were discussed. The present paper deals with the observations made with alkali tartrate by conductometric measurements. A summary with reference to the work done by various investigators on this issue had been included in Part I (*loc. cit.*). Although it was shown that copper reacted with alkali tartrate resulting in the formation of a complex containing metal and tartrate ion in the proportion of 1:1, no attempt was made to determine the stability of the complex formed. The author by utilising Job's method of continued variation (Job, *Compt. rend.*, 1925, 180, 928) has determined the instability constant of the complex.

### EXPERIMENTAL

Solutions prepared from Merck's copper nitrate and Rochelle salt (as alkali tartrate) were used in all the measurements. Both copper and tartrate were estimated iodometrically.

*Conductometric Measurements.*—The same apparatus, as in the case with tartaric acid (*loc. cit.*), was used in all the conductometric measurements. Conductometric titration results are shown in Tables I and II and in curves I and II (Fig. 1). Conductance measurements in both equi- and non-equimolecular solutions were made in the same way as in case with tartaric acid (*loc. cit.*). Tables III-V contain the experimental data for equimolecular and VI-IX for non-equimolecular solutions respectively. Curves I-III (Fig. 2) and I-IV (Fig. 3) demonstrate, as in the case with tartaric acid, the divergence from the additivity rule plotted against composition of the mixture in the case of equi- and non-equimolecular solutions respectively. In the case of equimolecular solutions, one experiment (Table IV; curve II, Fig. 2) was performed by taking ammoniacal solution of copper nitrate (*i.e.* ammonia was added to copper nitrate solution till the precipitate formed dissolved and then diluted to the required volume) instead of a simple solution.

During measurements, in the case of higher concentrations of copper and tartrate solutions (up to  $M/20$  strength), some mixtures in the neighbourhood of 1:1 became slightly turbid, if kept for some time. In those cases therefore readings were taken soon after mixing.

TABLE I

*Conductometric titration of copper nitrate with Rochelle salt (R-salt).*

*M/50-Copper nitrate (50 c.c.) solution was taken in a cell and molar R-salt added. Initial value of the conductance ( $\kappa/R$ ) of the copper nitrate solution =  $58.8 \times 10^{-4}$ . Temp. =  $30^\circ$ .*

(cf. Fig. 1, curve I),

R-salt soln. added.	Increase of conductance over the initial value after each addition.	R-salt soln. added.	Increase of conductance over the initial value after each addition.	R-salt soln. added.	Increase of conductance over the initial value after each addition.
0 c.c.	0	1.0 c.c.	$14.2 \times 10^{-4}$	2.0 c.c.	$56.1 \times 10^{-4}$
0.2	$3.7 \times 10^{-4}$	1.2	21.2	2.2	63.9
0.4	6.1	1.4	30.5	2.4	72.8
0.6	7.9	1.6	39.0	2.6	81.1
0.8	10.2	1.8	47.4	2.8	90.3

The increase in conductance, observed after each addition of R-salt solution over the initial value  $58.8 \times 10^{-4}$ , has been plotted against the ratio of copper to tartrate.

TABLE II

*Conductometric titration of copper nitrate with Rochelle salt (R-salt).*

*M/75-Copper nitrate solution (50 c.c.) was taken in a cell and molar R-salt solution added. Initial value of the conductance ( $\kappa/R$ ) of the copper nitrate solution =  $43.1 \times 10^{-4}$ . Temp. =  $30^\circ$ .*

(cf. Fig. 1, curve II).

R-salt soln. added.	Increase of conductance over the initial value after each addition.	R-salt soln. added.	Increase of conductance over the initial value after each addition.	R-salt soln. added.	Increase of conductance over the initial value after each addition.
0 c.c.	$0 \times 10^{-4}$	1.0 c.c.	$21.0 \times 10^{-4}$	2.0 c.c.	$65.6 \times 10^{-4}$
0.2	2.1	1.2	30.4	2.2	74.5
0.4	4.3	1.4	39.5	2.4	82.7
0.6	6.7	1.6	48.6	2.6	91.1
0.8	12.2	1.8	56.9	2.8	99.8

The increase in conductance observed after each addition of R-salt solution over the initial value  $43.1 \times 10^{-4}$  has been plotted against the ratio of copper to tartrate.

TABLE III

*Conductivity experiment of M/20-copper nitrate with M/20-Rochelle salt.*

Temp. = 30°. (cf Fig. 2, curve I).

Copper nitrate soln.	$(1/R) \times 10^4$ of the soln. in col. (1), each diluted to 50 c.c. = $C_1$ .	R-salt soln.	$(1/R) \times 10^4$ of the soln. in col. (3), each diluted to 50 c.c. = $C_3$ .	$(C_1 + C_3)$ = $C_5$	$(1/R) \times 10^4$ of the mix- ture of solns. in cols. (1) and (3) = $C_4$ .	$(C_3 - C_4)$ .
1	2	3	4	5	6	7
50 c.c.	138.9	0 c.c.	...	138.9	138.9	0
45	125.0	5	17.5	142.5	126.6	15.9
40	112.4	10	31.3	143.7	116.3	27.4
35	100.0	15	45.5	145.5	105.8	39.7
32.5	94.1	17.5	52.1	146.2	101.5	44.7
30	88.5	20	58.1	146.6	95.2	51.4
27.5	80.7	22.5	64.1	144.8	89.3	55.5
25	74.1	25	70.9	145.0	87.0	58.0
22.5	68.0	27.5	76.9	144.9	88.3	56.6
20	59.9	30	83.3	143.2	91.7	51.5
17.5	54.1	32.5	89.3	143.4	95.0	48.4
16.7	51.3	33.3	90.9	142.2	97.1	45.1
15	46.5	35	96.2	142.7	99.0	43.7
10	31.6	40	107.5	139.1	107.5	31.6
5	17.5	45	117.6	135.1	115.6	19.5
...	...	50	130.7	130.7	130.7	0

TABLE IV

*Conductivity expt. of M/20-Rochelle salt and M/20-copper nitrate (ammoniacal).*

Temp. = 30°. (cf Fig. 2, curve II).

Copper nitrate soln.	$(1/R) \times 10^4$ of the soln. in col. (1), each diluted to 50 c.c. = $C_1$ .	R-salt soln.	$(1/R) \times 10^4$ of the soln. in col. (3), each diluted to 50 c.c. = $C_3$ .	$(C_1 + C_3)$ = $C_5$ .	$(1/R) \times 10^4$ of the mixture of solns. in cols (1) and (3) = $C_4$ .	$(C_3 - C_4)$ .
1	2	3	4	5	6	7
50 c.c.	158.7	...	...	158.7	158.7	0
45	143.9	5 c.c.	17.5	161.4	149.3	12.1
40	129.9	10	32.3	162.2	139.9	22.3
35	115.6	15	47.2	162.8	133.3	29.3
32.5	108.7	17.5	53.8	162.5	130.7	31.8
30	100.0	20	60.6	160.6	128.2	32.4
27.5	93.5	22.5	67.1	160.6	126.1	34.5
25	87.0	25	74.1	161.1	125.0	36.1
22.5	79.4	27.5	80.0	159.4	125.8	33.6
20	70.9	30	87.0	157.9	126.6	31.3
17.5	61.4	32.5	93.2	154.6	127.8	26.8
15	54.1	35	99.0	153.1	129.0	24.1
10	38.0	40	111.1	149.1	131.1	18.0
...	...	50	135.1	135.1	135.1	0

TABLE V

*Conductivity experiment of M/30-Rochelle salt and M/30-copper nitrate*  
Temp. = 30°. (cf. Fig. 2, curve III).

Copper nitrate soln.	$(1/R) \times 10^4$ of the soln. in col. (1), each being diluted to 50 c.c. = $C_1$ .	R-salt soln.	$(1/R) \times 10^4$ of the soln. in col. (3), each being diluted to 50 c.c. = $C_2$ .	$(C_1 + C_2)$ = $C_3$ .	$(1/R) \times 10^4$ of the mix- ture of solns. in cols. (1) and (3) = $C_4$ .	$(C_3 - C_4)$ .
1	2	3	4	5	6	7
50 c.c.	95.2	0 c.c.	...	95.2	95.2	0
45	86.8	5	12.4	99.2	93.7	5.5
40	78.7	10	22.2	100.9	85.5	15.4
35	71.4	15	31.8	103.2	75.5	27.1
30	62.9	20	40.5	102.5	69.4	34.0
25	53.2	25	50.5	103.4	63.3	40.4
20	43.5	30	60.4	103.9	65.4	37.5
15	33.7	35	69.0	102.7	71.9	30.8
12.5	28.6	37.5	73.0	101.6	74.1	27.5
10	23.0	40	76.9	99.9	78.7	21.2
7.5	18.2	42.5	81.3	99.5	82.6	17.3
5	12.9	45	85.5	98.4	86.2	12.2
0	...	50	93.4	...	93.4	0

TABLE VI

*Conductivity experiment of M/20-copper nitrate and M/10-Rochelle salt.*  
Temp. = 30°. (cf. Fig. 3, curve I).

Copper nitrate soln.	$(1/R) \times 10^4$ of the soln. in col. (1), each diluted to 50 c.c. = $C_1$ .	R-salt soln.	$(1/R) \times 10^4$ of the soln. in col. (3), each diluted to 50 c.c. = $C_2$ .	$(C_1 + C_2)$ = $C_3$ .	$(1/R) \times 10^4$ of the mix- ture of solns. in cols. (1) and (3) = $C_4$ .	$(C_3 - C_4)$ .
1	2	3	4	5	6	7
50 c.c.	146.0	...	...	146.0	146.0	0
40	119.0	10 c.c.	62.5	179.5	121.2	58.3
35	105.3	15	89.3	194.6	123.5	71.1
33.3	97.8	16.7	99.7	197.5	124.2	73.3
32.5	95.2	17.5	104.7	199.9	125.0	74.9
31	94.3	19	111.1	205.4	129.4	76.0
30.5	93.2	19.5	113.6	206.8	130.2	76.6
30	91.7	20	116.3	208.0	131.6	76.4
27.5	85.2	22.5	130.7	215.9	144.9	71.0
25	76.9	25	140.8	217.7	152.7	65.0
22.5	71.4	27.5	155.0	226.4	162.6	63.8
20	64.5	30	166.7	231.2	173.9	57.3
15	49.0	35	190.5	239.5	190.5	49.0
10	33.9	40	212.8	251.8	215.1	36.7
...	...	50	259.7	259.7	259.7	0

TABLE VII

*Conductivity experiment of M/30-copper nitrate and M/10-Rochelle salt.*

Temp. = 30°. (cf. Fig. 3, curve II).

Copper nitrate soln.	$(1/R) \times 10^4$ of the soln. in col. (1), each diluted to 50 c.c. = $C_1$ .	R-salt soln.	$(1/R) \times 10^4$ of the soln. in col. (3), each diluted to 50 c.c. = $C_3$ .	$(C_1 + C_3) = C_5$ .	$(1/R) \times 10^4$ of the mixture of solns. in cols. (1) and (3) = $C_4$ .	$(C_3 - C_4)$ .
1	2	3	4	5	6	7
50 c.c.	98.0	—	—	98.5	98.5	0
40	80.7	10 c.c.	61.4	142.1	92.6	49.5
37.5	75.8	12.5	74.6	150.4	94.3	56.1
35	71.4	15	88.5	159.9	101.0	58.9
33.5	69.9	16.5	97.1	167.0	107.5	59.5
33	68.7	17	100.0	168.7	108.7	60.0
32.5	67.8	17.5	102.0	169.8	110.5	59.3
30	62.5	20	114.3	176.8	120.5	56.3
27.5	58.8	22.5	126.6	185.4	131.6	53.8
25	54.1	25	138.9	193.0	144.9	48.1
20	43.9	30	162.6	206.5	166.7	39.8
15	33.9	35	183.5	217.4	185.9	31.5
10	23.8	40	206.2	230.0	208.3	21.7
—	—	50	250.0	250.0	250.0	0

TABLE VIII

*Conductivity experiment of M/50-copper nitrate and M/10-Rochelle salt.*

Temp. = 30°. (cf. Fig. 3, curve III).

Copper nitrate soln.	$(1/R) \times 10^4$ of the soln. in col. (1), each diluted to 50 c.c. = $C_1$ .	R-salt soln.	$(1/R) \times 10^4$ of the soln. in col. (3), each diluted to 50 c.c. = $C_3$ .	$(C_1 + C_3) = C_5$ .	$(1/R) \times 10^4$ of the mixture of solns. in cols. (1) and (3) = $C_4$ .	$(C_3 - C_4)$ .
1	2	3	4	5	6	7
50 c.c.	60.6	0 c.c.	—	60.6	60.6	0
45	55.6	5	31.3	86.9	62.5	24.4
40	51.3	10	59.5	110.8	71.4	39.4
37.5	48.3	12.5	74.6	122.9	80.0	42.9
36.5	47.4	13.5	80.0	127.4	83.3	44.1
36	47.0	14	82.6	129.6	85.2	44.4
35.5	46.3	14.5	84.8	131.1	87.0	44.1
35	45.7	15	87.0	132.7	89.3	43.4
32.5	42.6	17.5	101.0	143.6	102.0	41.6
30	39.2	20	111.1	150.3	111.1	39.2
25	33.0	25	134.2	167.2	131.6	35.6
20	27.0	30	160.0	187.0	156.2	30.8
10	14.7	40	200.0	214.7	198.0	16.7
0	—	50	232.6	232.6	232.6	0

TABLE IX

Conductivity experiment of  $M/40$ -copper nitrate and  $M/16$ -Rochelle salt.Temp. =  $30^\circ$ . (cf. Fig. 3, curve IV).

Copper nitrate soln.	$(1/R) \times 10^4$ of the soln. in col. (3), each diluted to 50 c.c. = $C_1$ .	R-salt soln.	$(1/R) \times 10^4$ of the soln. in col. (3), each diluted to 50 c.c. = $C_2$ .	$(C_1 + C_2) = C_3$ .	$(1/R) \times 10^4$ of the mixture of solns. in cols. (1) and (3) = $C_4$ .	$(C_3 - C_4)$ .
1	2	3	4	5	6	7
50 c.c.	75.2	0 c.c.	—	75.2	75.2	0
40	60.6	10	38.5	99.1	67.6	31.5
35	53.5	15	55.6	109.1	68.0	41.1
32.5	50.5	17.5	64.5	115.0	72.5	42.5
31.5	48.5	18.5	69.0	117.5	74.1	43.4
30	46.5	20	74.1	120.6	76.9	42.1
27.5	43.5	22.5	81.3	124.8	84.8	40.0
25	40.0	25	87.7	127.7	91.7	36.0
22.5	36.8	27.5	94.3	131.1	99.0	32.1
20	32.7	30	103.1	135.8	105.3	30.5
15	25.3	35	119.0	144.3	119.0	25.3
10	15.2	40	132.5	147.7	132.5	15.2
—	—	50	172.4	172.4	172.4	0

## DISCUSSION

It is observed from the conductometric titration curves (curves I-II, Fig. 1) that a sharp break occurs in the proportion of 1:1. Therefore it can be concluded that the reaction occurs in that proportion. The same conclusion is also supported by the results of conductance measurements of equimolecular solutions at various concentrations in which a maximum is obtained in each case in that proportion when the divergence from the additivity rule due to complex formation is plotted against composition of the mixture (curves I-III, Fig. 2).

FIG. 1

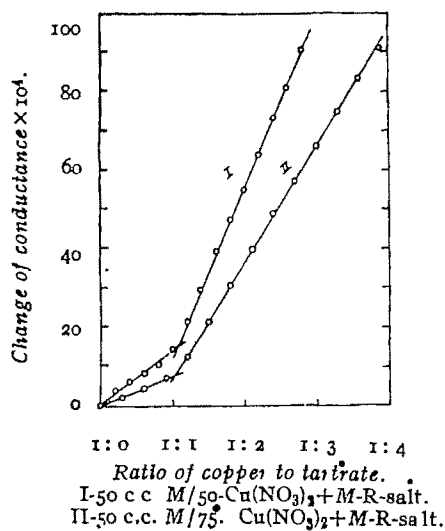
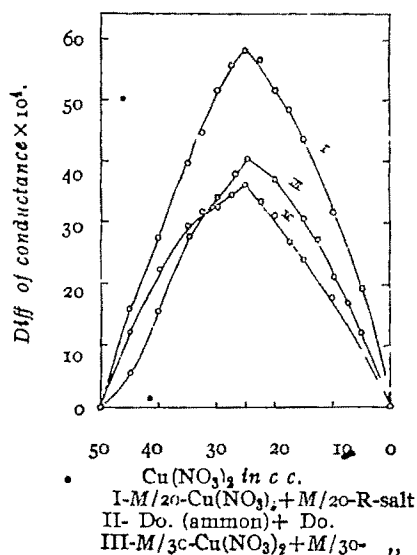


FIG. 2



From the experimental results therefore it can be definitely concluded that in dilute solution one and only one complex is formed between cupric and tartrate ion ( $\text{Cu}^{++} + \text{T}'' \rightleftharpoons \text{CuT}$ , where  $\text{T}''$  = tartrate ion) and that in the proportion of 1 : 1.

Now by applying Job's method of continued variation (*loc. cit.*) the instability constant can be found out from the measurement of conductance in non-equimolecular solutions.

#### Calculations of $K$ , the Instability Constant

The equation relating to value of  $K$  is given by

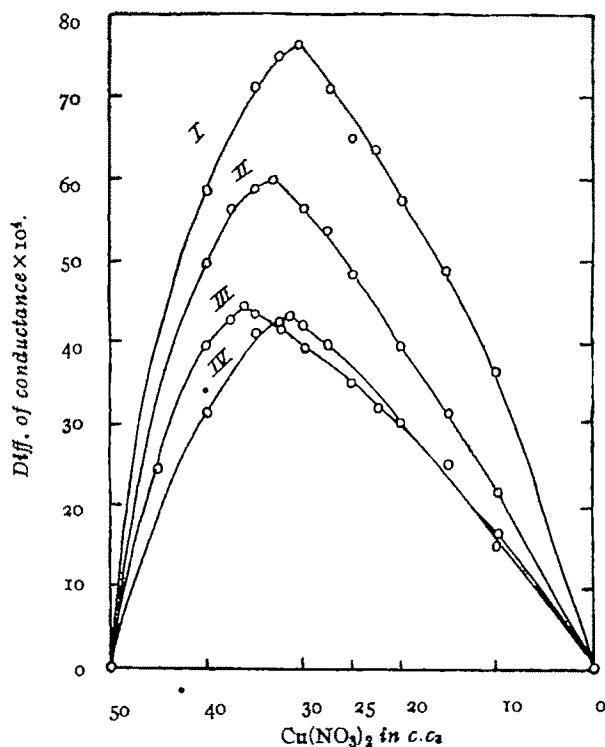
$$K = \frac{C \{(p+1)x-1\}^2}{(p-1)(1-2x)}$$

where  $C$  is the molar concentration of copper nitrate,  $p$ , the molar concentration of Rochelle salt (R-salt) and  $x$  c.c. of R-salt reacting with  $(1-x)$  c.c. of copper nitrate to give the maximum effect.

TABLE X

Table No.	Fig. No.	Curve No.	$C$ .	$p$ .	$x$ .	$K \times 10^3$ .	Mean $K \times 10^3$ .
VI	3	I	0.050	2	0.39	6.6	
VII	3	II	0.033	3	0.34	6.7	
VIII	3	III	0.020	5	0.28	5.3	6.1
IX	3	IV	0.025	2.5	0.37	5.8	

FIG. 3



Curves I-IV refers respectively, to  $M/20\text{-Cu}(\text{NO}_3)_2 + M/10\text{-R-salt}$ ,  $M/30\text{-Cu}(\text{NO}_3)_2 + M/10\text{-R-salt}$  and  $M/50\text{-Cu}(\text{NO}_3)_2 + M/16\text{-R-salt}$ .



Although the complex formed in the case of tartaric acid and alkali tartrate is the same ( $\text{CuT}$ ), there is some divergence in the value of  $K$  as obtained in the two cases. The value in the former case (with tartaric acid) is  $9.6 \times 10^{-3}$  and in the latter (with alkali tartrate)  $6.1 \times 10^{-3}$ . This variation is due to the fact, as has already been discussed (Part I, *loc. cit.*), that the neutral complex formed is less stable in presence of free hydrogen ion liberated by the reaction in case with tartaric acid and as a result the stability is affected by the presence of free hydrogen ion. It is observed that nature of the conductometric titration curves with tartaric acid and alkali tartrate differs considerably. In case of the former a rather continuous curve is obtained, whereas in the latter case a well defined break signifies the complex formation.

The observations from absorption measurements with alkali tartrate will be the subject matter of the next paper.

The author wishes to offer his best thanks to Prof. P. B. Sarkar, D. es. Sc., of the University College of Science and Technology, Calcutta for the valuable discussions, to Dr. A. K. Majumdar, Professor of Inorganic Chemistry, College of Engineering and Technology, Jadavpur, for taking keen interest.

INORGANIC CHEMISTRY LABORATORY,  
COLLEGE OF ENGINEERING AND TECHNOLOGY, BENGAL,  
JADAVPUR, CALCUTTA.

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## DURABILITY OF SODA-LIME-SILICATE GLASSES. PART V. EFFECT OF ULTRAVIOLET RADIATIONS ON CHEMICAL DURABILITY

BY H. N. DAS GUPTA AND AMALENDRA NATH CHOWDHURY

Effect of long and short waves of ultraviolet rays on durability of chilled glass has been studied and the chemical durability of glass in bulk is attended with some definite increase as a result of the effect with a decrease in the surface resistivity.

It is well known that long-wave ultraviolet rays penetrate ordinary glass and quartz, while short-wave rays penetrate quartz, but are completely absorbed by ordinary glass. In the present communication the effect of ultraviolet rays of both long and short waves on the chemical durability of chilled glass has been studied. It will be evident from the experimental portion that when unannealed or chilled glass is exposed to these radiations, whether of short or of long wave-lengths, there is some definite increase in the chemical durability of glass in bulk. The surface resistivity, however, is found to decrease, indicating thereby an increased surface alkalinity. In this respect the effect has been found to be analogous to that of annealing (cf. Williams and Weyl, *Glass Ind.*, 1945, **28**, 275, 325; Sen, Chowdhury and Das Gupta, this *Journal*, 1949, **26**, 379). The chemical resistivity of glass is expressed as the solubility of alkali and, as such, the determination of durability of glass was made by taking recourse to "power test" (Faraday, *Phil. Tans.*, 1830, p. 49; Pelouze, *Compt. rend.*, 1856, **43**, 117; Mylius and Foerster, *Ber.*, 1889, **22**, 1092; *Z. Instrum.*, 1889, **9**, 120; Hagmaier, *Met. Chem. Eng.*, 1917, **16**, 604; Nicolardot, *Compt. rend.*, 1919, **169**, 335; Peddle, *J. Soc. Glass Tech.*, 1920, **4**, 3, 299; 1921, **5**, 72, 195).

In Part IV of the present series (Chowdhury and Das Gupta, this *Journal*, 1949, **26**, 425) it has been observed that soda-lime-silicate glass, whether chilled or annealed, when subjected successively to powder test after intervals of 24 hours each, gives residual sulphuric acid values (R. S. A. V.) of descending magnitude and up to a restricted number of times. Similar R. S. A. Vs are also obtainable with glass exposed to ultraviolet radiations (Table VII).

A prospecting set for fluorescent minerals, designed by Fraser and Chalmers (*Trans. Inst. Min. Met.*, Vol. L1V, 1944-45), was used as a source of short-wave ultraviolet rays. From this set about 25% of the total input energy is emitted as radiation, the distribution of which is approximately as shown in Table III. For longer waves ultraviolet lamp was used. The analysis of the radiation from such a lamp is given in Table IV.

Four different specimens of glass were exposed to ultraviolet radiations. Three such specimens of different compositions were prepared in the laboratory, while the other sample, blown in the form of a bottle, was procured from a firm at Howrah. This was not allowed to anneal. The effect of longer exposure on durability of glass could not, however, be studied owing to restriction in respect of continuous running of the appliances for the ultraviolet radiations.

## E X P E R I M E N T A L

Three new glasses of different compositions were melted and plained in the usual way, in separate Morgan crucibles. Each was withdrawn, while white hot, from the furnace and was cooled rapidly. Lumps of moderate thickness were used for different exposures. Table I gives the purity of the ingredients used, and Table II shows the percentage batch composition.

TABLE I

Material.	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO	Na <sub>2</sub> O.	Loss.
Sand ...	97.3%	0.31%	1.6%	0.39%	Trace	...	0.29%
Lime ...	1.85	0.75	2.68	70.99	Trace	...	23.8
Soda ash ...	0.29	...	...	S. trace	S. trace	48.76%	16.2

TABLE II

Batch No.	SiO <sub>2</sub> .	CaO.	Na <sub>2</sub> O.
A	74%	11.5%	14.5%
B	74	10	16
C	68	10	22

TABLE III

*Distribution of U. V. radiation from the prospecting set.*

Type of radiation.	Distribution of radiation (output)					
Short-wave U. V. (2537 Å) ...	...	...	...	...	...	60%
Long-wave U. V. (3132 and 3650 Å) ...	...	...	...	...	...	10
Visible light ...	...	...	...	...	...	25
Near infra-red ...	...	...	...	...	...	5
						Total 100

TABLE IV

*Analysis of radiation from the lamp.*

Wave-length.	Rel. comp. of the U. V. radiation.	Wave-length.	Rel. comp. of the U. V. radiation.
4040 Å	2.7%	3340 Å	4.5%
3650	91.0	3130	1.8
			Total 100

For each exposure, lumps weighing approximately 15 g. were taken. The source of radiation was practically in contact with the glass lump in every case. Powder test was made in the usual way after exposing the sample for 1 or 1½ hour. Exposure for shorter period was avoided as this did not give comparative results. In order to test

the effect of radiation on surface durability of glass, lumps were powdered to pass 150 mesh to increase the total surface area. This powder was then exposed to radiations. The results of "powder test" obtained after exposure to short-wave radiation have been incorporated in Table V and those of long-wave in Table VI.

TABLE V

*Sulphuric acid value after exposure to short-wave U. V. radiation.*

Specimen.	S. A. V. of chilled sample.	Form in which exposed.	Duration of exposure.	S. A. V. after exposure.
Howrah glass	2125.4	Powder	1 hour	2222.7
	2130.9			2230.2
		Lump	1 "	2032.5
				2029.6
B	509.2	Powder	1 "	594.2
	500.0			594.6
		Lump	1 "	431.9
				434.1

TABLE VI

*Effect of long-wave U. V. radiation.*

Specimen.	S. A. V. of chilled sample.	Form in which exposed.	Duration of exposure.	S. A. V. after exposure.
Howrah glass	2125.4	Powder	1 hr.	2197.2
	2130.9			2194.5
		Lump	1	2023
				2019
A	250.5	Do	1	215.1
	261.4			218.1
		Do	1	197.1
				195.8
C	1285.1	Lump	1	1184
	1280.6			1193
		Do	1	1039.1
				1032.5
		Powder	1	1318.7
				1325.3

It will then be clear from Tables V and VI that the surface durability of glass definitely decreases due to such exposures. Table VII gives the results of residual sulphuric acid values.

TABLE VII

Specimen	Duration (days).	R. S. A. V.	Specimen.	Duration (days)	R. S. A. V.
Howrah glass	1	1259.5	A	1	62.4
	2	808.7		2	41.3
	3	421.3		3	15.7
	4	270.3		4	Nil
	5	190			

## DISCUSSION

No decisive conclusion regarding the effect of ultraviolet radiations on glass could be arrived at, pending collections of further facts. However, a tentative suggestion is put forward.

In a communication Moore (*J. Soc. Glass Tech.*, 1949, **33**, No. 154, pp. 265-275) has suggested, on theoretical grounds, that the condition in molten alkali-lime-silica glasses will tend towards reduction rather than oxidation. According to him the tendency of reduction to occur is due (a) to thermal instability of many peroxides (and certain oxides) at the temperatures used in melting glasses, and (b) to temporary combination of loosely held oxygen atoms with the alkali ions diffusing through the glass. Evidence, bearing on the above mentioned deduction, has actually been collected by Moore and Prasad (*ibid.*, 1949, **33**, No. 155, pp. 336-70), after investigating spectro-photometrically the colours given by iron in glasses of alkali-lime-silica and alkali-lime borosilicate types.

Accepting the views of Moore, it is to be expected that in a molten glass the alkali metal is largely ionised and, as such, the condition represented by  $\equiv\text{Si-O}^-$  and  $\text{Na}^+$  must exist, at any rate to a large extent, even if all the alkali atoms are not ionised. The alkali ions diffuse through the glass at rates depending on temperature and it is proposed that the "natural alkalinity" of chilled glass is due to this. When, however, a chilled glass, in bulk, is exposed to the influence of ultraviolet radiations, perhaps strengthening of the bond between the alkali ion and the anionic net-work is brought about. This imparts an increased durability to glass in bulk. The total surface area of the same weight of powdered glass is undoubtedly considerable. At the surface, however, the alkali metals appear to be under two-fold influences, viz., (a) of radiations, and (b) of weathering agent, the effect of one being opposite to that of the other. During exposure appreciable quantity of ozone formation takes place. The ozone perhaps exerts its weathering influence on alkali metal on the surface and offsets the effect of ultraviolet radiations. If this assumption be correct, we should naturally expect decreased durability by such exposures. Further work in this line is in progress.

DEPARTMENT OF APPLIED CHEMISTRY,  
UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,  
CALCUTTA  
AND  
DEPARTMENT OF CHEMISTRY, FUELS AND METALLURGY,  
INDIAN SCHOOL OF MINES & APPLIED GEOLOGY,  
DHANBAD.

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## STUDIES ON RANCIDITY OF BUTTERFAT. PART IX. THE ACTION OF METALS

BY S. MUKHERJEE

Of the metals tested, copper and iron are the strongest pro-oxidants. Tin and aluminium are relatively ineffective. The metallic soaps are stronger pro-oxidants than the corresponding metals, and when the metal is supplied in an aqueous phase in contact with fat, the rate is much slower. In absence of oxygen, the catalytic effect of the metals on the oxidation of the fat is not observed.

The pro-oxidant effect of certain metals, notably copper and iron, upon oils and fats has been known for many years, but the available information has been scattered and sometimes incomplete to be of much help to the fat industry. The relative activities of various common metals and alloys in accelerating rancidity is a matter of considerable practical importance, since the choice of material for construction of the processing plant, storage vessels and containers will largely depend on it. A brief resumé of the present state of knowledge concerning the behaviour of metals is given below.

Golding and Feilman (*J. Soc. Chem. Ind.*, 1905, **24**, 1285) observed that a "tallowy" odour developed in milk that was passed over a tinned copper cooler from which part of the plating had been worn away in use; moreover, contact with copper or brass or in less degree with iron was found to produce "tallowy" odour in butter (Hunziker and Hosman, *J. Dairy Sci.*, 1918, **1**, 320). Very recently Paul, Bhalerao and Ananta-krishnan (*Ind. J. Dairy Sci.*, 1949, **2**, 7) have carried out experiments on the storage of ghee in different types of containers. An attempt at correlation of the nature of particular metal with its solubility in weak organic acids in producing off-flavours in milk-products has been made by using different metallic equipments in creameries (Hunziker, Cordes and Niseen, *J. Dairy Sci.*, 1929, **12**, 179). It was evaluated, from the measurement of the length of time necessary to produce rancidity in the cases of corn and cotton-seed oils and lard, when strips of metals were immersed in them, that copper was the most and tin and aluminium were the least active of the metals studied (Emery and Henley, *Ind. Eng. Chem.*, 1922, **14**, 937). Metallic oleates accelerated the bleaching of vegetable oils at 80° in descending order of efficiency in the series : Co, Mn, Cu, Ni, Pb and Fe (Rai, *J. Soc. Chem. Ind.*, 1917, **36**, 948). The addition of a soluble copper salt (Cu-stearate) at a concentration of 1 to 2 parts per million was shown to greatly increase the rate of peroxide formation in lard at 100° (King, Roschen and Irwin, *Oil & Soap*, 1933, **10**, 105). A few similar experiments have also been done with milk and butter. Excepting these instances practically the whole of the published work has been concentrated on the effect of the addition of metals and salts to dry oils and fats, whereas most foodstuffs contain in addition to the fat an aqueous phase containing non-fatty materials. Lea (*J. Soc. Chem. Ind.*, 1936, **55**, 293T) studied the effect of certain metallic salts dissolved in aqueous phase in contact with lard and

observed that extremely minute amounts often had a marked influence on the rate of onset of rancidity which increased with the concentration of the metal.

The present study on the action of metals on fats has been divided into three sections :

- (i) Action of metals in metallic form studied by storage experiments in different metallic containers.
- (ii) Action of metals in solution, storage experiments carried out in pyrex glass vessels with addition of different metallic oleates.
- (iii) Addition of metals in aqueous solution, the effect of addition of water-soluble metallic salts (as sulphates) dissolved in aqueous phase in contact with butterfat

The experimental results are summarised in Tables I, II and III.

TABLE I

*Effect of storage of butterfat in different metallic containers.*

Expt No.	Metal.	Peroxide and Kreis values after							
		15 days.		30 days.		45 days.		60 days.	
		P. V.	K.	P. V.	K.	P. V.	K.	P. V.	K.
1.	Aluminium	0.20	1.3	1.0	2.5	6.3	3.4	11.0	9.7
2.	Copper	0.50	2.0	9.3	17.4	28.7	27.0	33.1	20.0
3.	Iron	0.20	1.4	1.2	2.3	7.2	5.1	23.3	12.0
4.	Lead	0.27	1.4	1.1	2.5	7.2	4.5	20.0	10.5
5.	Nickel	0.5	1.4	1.8	2.8	7.3	6.1	21.4	15.0
6.	Tin	0.17	1.1	1.3	2.4	3.7	3.2	7.0	7.4
7.	Zinc	0.27	1.2	1.0	1.6	8.3	3.9	10.3	8.4
8.	Control	0.14	0.1	1.1	1.6	2.4	4.2	3.2	8.8

TABLE II

*Effect of storage of butterfat in presence of metals in solution (as oleates).*

Expt No.	Substance.	Conc. (p.p.m.)	Peroxide and Kreis values after							
			15 days.		30 days.		45 days.		60 days.	
			P. V.	K.	P. V.	K.	P. V.	K.	P. V.	K.
1.	Cobalt oleate	1	0.54	2.0	2.2	4.0	4.8	5.4	18.6	12.0
2.	Copper oleate	5	1.50	3.8	5.6	6.6	18.4	10.0	30.0	20.6
3.	Lead oleate	5	0.72	2.6	2.6	5.2	10.6	9.0	22.2	14.0
4.	Manganese oleate	5	0.72	2.1	2.2	4.2	4.6	6.4	12.8	10.2
5.	Iron oleate	5	1.0	2.6	3.2	5.6	8.4	9.8	19.5	21.0
6.	Nickel oleate	5	0.54	1.0	2.0	4.1	7.4	5.5	19.0	10.0
7.	Control	—	0.14	0.1	1.3	1.6	2.4	4.2	3.0	8.8

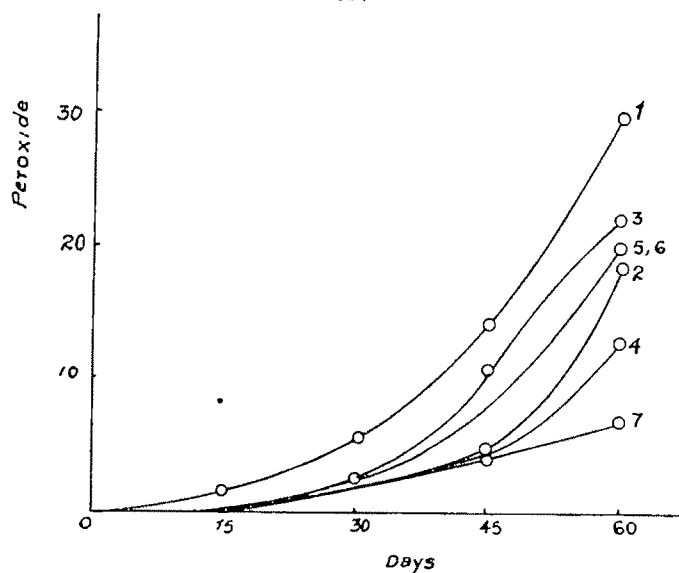
TABLE III

*Effect of metals in aqueous phase in contact with butterfat on rancidity.*

Expt No.	Metal	Conc. (p.p.m.)	Peroxide and Kreis values after							
			15 days.		30 days		45 days.		60 days.	
			P.V.	K.	P.V.	K.	P.V.	K.	P.V.	K.
1.	Aluminium	25	0.22	1.1	0.93	2.2	2.0	2.2	3.0	2.4
2.	Chromium	"	0.24	1.7	0.98	2.3	2.3	3.2	5.4	5.4
3.	Copper	"	0.40	1.5	3.70	4.8	14.6	10.5	23.1	13.0
4.	Iron	"	1.20	3.2	8.7	7.2	16.6	12.4	30.3	18.4
5.	Nickel	"	0.27	1.0	0.5	1.2	1.9	2.2	2.2	2.2
6.	Zinc	"	0.10	0.3	0.96	1.2	1.9	2.0	3.0	2.7
7.	Control	—	0.20	0.3	1.89	—	2.4	—	3.55	—

It would appear from these tables that copper and iron are in general the strongest pro-oxidants of rancidity of butterfat, whether in metallic state or dissolved in the form of fatty acid soaps or present in solution in water phase in contact with the fat. Desirable results were obtained with tin, aluminium and zinc, and hence for all practical purposes tinned vessel may safely be used as materials for construction of the containers. Of the oleates studied, nickel is the least effective, although in general they are all pro-oxidants (Fig. 1). The samples stored in copper containers acquire a bluish green colour. In most of the samples, the yellow colour is completely bleached on storage.

FIG. 1



Curves 1—6 refer respectively to oleate of Cu, Co, Pb, Mn, Fe and Ni, and curve 7 refers to Control.

A close examination of the tables reveals that increase in autoxidation rate of fats by the metals possibly takes place by first dissolution of the metals in the fats by the free acids with formation of the soluble salts and these fatty acids soaps of the metals are the active catalysts in the process. When the metal is in the aqueous phase, the slower rate observed is possibly due to the slow rate of diffusion of the metallic ion



from the aqueous to the fat phase. The rate is maximum when the metal is provided in the form of the soluble salt, viz. the oleate. With the experiments on storage in the metallic containers the formation of peroxides at the end of 15 days is much smaller than in the experiments with the oleates, because in the first case a certain time must elapse before the free fatty acids are formed to attack the metallic containers and form the highly active soaps.

The effectiveness of a particular metal in accelerating the production of rancidity in the fats of foods brought in contact with it thus depends on the combined effect of surface activity, solubility and accelerating effect of the dissolved metal. This can be seen from the more accelerated behaviour of the metallic oleates in comparison with the metals themselves.

Next, it was considered important to study the effect of metals in absence of oxygen, with a view to observing its effectiveness in bringing out rancidity under anaerobic conditions. The results of the experiments are given in Table IV.

TABLE IV

*Action of metals in presence and absence of oxygen on the development of rancidity in butterfat.*

Expt. No.	Description.	Peroxide values after			
		15 days.	30 days	45 days.	60 days.
1.	Control in air	0.1	1.3	2.4	3.0
2.	Copper oleate (5 p.p.m.) in presence of $O_2$	1.50	5.6	18.4	30.0
3.	Copper oleate (5 p.p.m.) in absence of $O_2$	0.0	0.0	0.0	0.25
4.	Cobalt oleate (5 p.p.m.) in presence of $O_2$	2.5	7.2	22.9	36.2
5.	Cobalt oleate (5 p.p.m.) in absence of $O_2$	—	—	0.0	0.15

From the results in Table IV it can be concluded that the harmful effect of the metals on fat is due to an acceleration of the normal process of oxidation; in absence of oxygen they are unable to produce this effect. A trace of an active metal added to the fat will reduce and may in some cases destroy the induction period of butterfat (Expt. 2, Table IV).

From the above results it appears that there exists no simple relation between the chemical properties of metals and their activities as accelerators of fat oxidation, but the generalisation of Mackey and Ingle seems to be useful as a rough guide. According to these authors, "in its oil soluble form a metal which exists in more than one state of oxidation acts as a drier or oxygen-carrier, provided that the salts of the lower oxides are more stable than the higher. The more oxides a metal can form, the greater is its catalytic power" (Mackey and Ingle, *J. Soc. Chem. Ind.*, 1916, **35**, 454).

## STUDIES ON RANCIDITY OF BUTTERFAT. PART X. THE INFLUENCE OF OXYGEN CONCENTRATION ON RANCIDITY

BY S. MUKHERJEE

The effect of pressure of oxygen on the development of rancidity is comparatively insignificant. Relatively small amounts of dissolved oxygen present in fats and oils exert a strong influence on the rancidity. Rancidity by the formation of peroxides of the unsaturated glycerides proceeds in a limited supply of oxygen, which is followed by complete decomposition of the peroxides resulting in the formation of aldehydes at advanced stages. The dissolved oxygen in the fat samples has been measured with the help of van Slyke's apparatus

The role of oxygen as the fundamental initiator of the process of rancidity in fat has been demonstrated beyond all doubts in the previous papers in the series. The next thing of importance is the concentration of oxygen on the rate of oxidation of fats.

The effect of pressure of oxygen, especially low pressure, on the rate of oxidation of fats is of particular interest because of the present tendency towards storage of fat-containing foodstuffs of various kinds in hermetically sealed containers either under vacuum or inert atmospheres with the obvious object of preventing oxidative rancidity. Unfortunately no work on the effect of pressure of oxygen on the rate of oxidation of fats has yet been published. The present investigation has been devoted to the study of the effect of varying concentration of oxygen within wide limits. The experiments have been divided into (a) effect of pressure of oxygen on the development of rancidity and (b) development of rancidity in limited oxygen supply.

### EXPERIMENTAL

#### *Effect of Pressure of Oxygen*

The effect of oxygen concentration of the atmosphere of storage in conical flasks, fitted with corks with inlet and outlet tubes connected with stop-cocks was studied. The air in the flasks was displaced by mixtures of oxygen and nitrogen, prepared in desired proportions to give different oxygen concentrations in different aspirator bottles, the passage of the gas being made for sufficiently long time to ensure complete displacement after the flasks had first been evacuated for a short time by means of a high vacuum pump. This study was again divided into two sections: (i) effect of high oxygen pressure, viz. above atmospheric concentration and (ii) effect of low oxygen pressure, viz. below atmospheric concentration. The respective concentrations used were 30%, 40%, 50%, 60%, 75%, 90% and 100% and 15%, 10%, 5%, 3%, 2% and 1%. The progress of rancidity was followed by the determination of Kreis and peroxide values at regular intervals. The gas mixture was replenished fortnightly after each determination in order to keep the concentration constant throughout the experiment. The samples

were stored in a thermostat at 38°. The results are given in Tables I and II and some of these results are shown graphically in Fig. 1. The results of each concentration was checked with duplicate experiment and the mean values are recorded, the variation between the values lying within 5%.

TABLE I

*Effect of low oxygen pressure on the development of rancidity in butterfat at 38°.*

Expt. No.	Oxygen conc.	Peroxide and Kreis values after									
		15 days.		30 days.		45 days.		60 days.		80 days.	
		P.V.	K.	P.V.	K.	P.V.	K.	P.V.	K.	P.V.	K.
1.	Control of air	0.14	0.1	1.10	1.6	2.4	4.2	3.0	8.8	8.0	10.5
2.	15%	0.14	0.2	1.10	1.6	2.35	4.0	2.5	5.0	6.5	7.9
3.	10	0.14	0.2	1.10	1.6	2.20	3.9	2.4	4.6	6.0	7.0
4.	5	0.14	0.2	1.10	1.58	2.1	3.9	2.3	4.6	4.3	7.0
5.	3	0.14	0.2	1.10	1.58	2.0	3.8	2.3	4.4	3.2	6.5
6.	2	0.14	0.2	1.10	1.58	2.0	3.6	2.3	4.2	3.2	6.5
7.	1	0.14	0.2	1.10	1.58	2.0	3.6	2.2	4.0	3.0	6.6

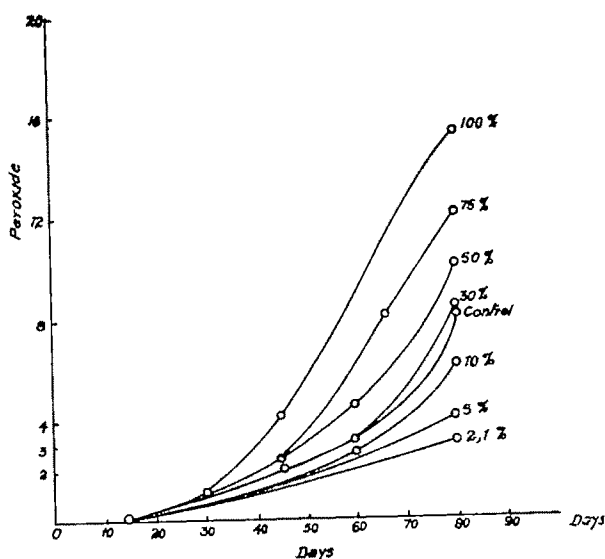
TABLE II

*Effect of high oxygen pressure on the development of rancidity in butterfat on storage at 38°.*

Expt. No.	Oxygen conc.	Peroxide and Kreis values after									
		15 days.		30 days.		45 days.		60 days.		80 days.	
		P.V.	K.	P.V.	K.	P.V.	K.	P.V.	K.	P.V.	K.
1.	Control in air	0.14	0.1	1.0	1.6	2.4	4.2	3.0	8.8	8.0	10.5
2.	30%	0.14	0.1	1.0	1.6	2.4	4.5	3.30	9.0	8.2	11.0
3.	40	0.14	0.1	1.0	1.6	2.4	5.0	3.87	9.6	9.6	12.0
4.	50	0.14	0.1	1.1	1.65	2.4	5.1	4.12	10.0	10.2	14.0
5.	60	0.14	0.1	1.1	1.85	2.45	6.0	5.4	12.0	12.05	16.2
6.	75	0.14	0.1	1.25	2.0	2.5	6.0	8.0	12.5	12.0	18.1
7.	90	0.14	0.1	1.25	2.0	4.0	6.0	8.15	12.6	12.1	18.0
8.	100	0.14	0.1	1.25	2.1	4.0	7.5	8.5	13.1	15.0	18.1

The effect of decreasing the oxygen content of the atmosphere of storage was found to be almost without effect on the induction period of the fat, i. e. fat stored in air as also in an atmosphere of air diluted with different volumes of nitrogen, showed identical induction periods, but the rate of subsequent oxidation was greater in air (Table I).

FIG. 1



The effect of increasing the oxygen concentration from 2.1% to 100% is that the induction period very nearly remains constant till the atmosphere is completely replaced by one of pure oxygen. The general effect is that the rate of subsequent oxidation has been increased but the results are not so well defined as to distinguish between the various concentrations.

The amount of oxygen required to bring a fat, particularly one like butterfat, containing relatively low proportions of acids, less saturated than oleic, to the end of induction period is very small. It is thus possible that reduction in the pressure of oxygen over a considerable range may produce much less than a proportionate decrease in the oxidation during the induction period. Moreover, the rate of oxidation during this period is controlled by natural antioxidants present in the fat. So also by varying the pressure of oxygen from 2.1-100%, one fails to obtain a proportionate increase in the oxidation rate, although once the induction period is over the oxidation rate seems to increase somewhat due to an increased concentration of oxygen.

#### *Development of Rancidity in Limited Oxygen Supply*

In experiments conducted above, free access of oxygen to the fat was assured. It is of interest to study the case when the total quantity of oxygen available is less than that which can be used up by the fat. For this purpose, the following experiments were conducted:—

(i) Storage of butterfat in a large sealed tube (about 150 c.c. capacity) over a small volume of oxygen.

(ii) Storage in vacuum.

(iii) Storage in inert gas ( $N_2$ ).

(iv) Storage of butterfat in a large test tube (50 c.c.) completely filled with fat and kept stoppered with a velvet cork, and subsequently sealed with wax.

The mean value of the results of experiments carried out in duplicate are tabulated below (Table III) and graphically in Fig. 2

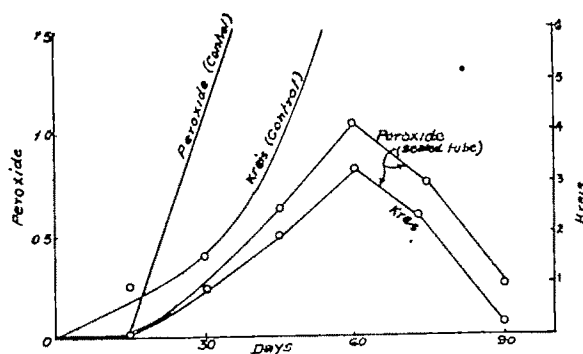
TABLE III

*Development of rancidity of butterfat in limited oxygen supply.*

Expt. No.	Description.	Peroxide and Kreis values after											
		15 days.		30 days.		45 days.		60 days.		75 days.		80 days.	
		P.V.	K.	P.V.	K.	P.V.	K.	P.V.	K.	P.V.	K.	P.V.	K.
1.	Stored in sealed tube (i)	0	0	0.35	1.0	0.65	2.0	1.04	3.3	0.74	2.4	0.25	0.2
2.	Stored in vacuum (ii)	—	—	—	—	—	—	—	—	0.08	0.80	0.2	1.0
3.	Stored in N <sub>2</sub> (iii)	0	0	0.30	1.0	0.60	2.1	1.04	3.2	1.2	4.2	2.0	5.1
4.	Stored in a completely filled test tube (iv)	0	0	0.2	0.8	0.52	2.0	1.0	3.0	0.8	2.7	0.56	0.8
5.	Control in air	0.14	0.1	1.1	1.6	2.4	4.2	3.2	8.8	15.0	10.2	2.30	13.4

It is evident from the above table that the formation of peroxide is very much depressed as compared to the control sample in air. The development of peroxide, however, proceeds slowly with time but after a certain maximum is reached, the peroxide content gradually falls off as the free oxygen is consumed (cf. Fig. 2); secondary changes set in resulting in the decomposition of peroxides. Formation of substance responsible for Kreis test proceeds in the fat stored in a limited oxygen supply until most of the latter and peroxide have been used up. Decomposition by secondary reaction results in a fall and almost total disappearance of the Kreis test (Fig. 2).

FIG. 2



That the fat still tastes rancid after storage in limited oxygen supply even after most of the peroxides and Kreis-active substances have undergone decomposition, seems to indicate that volatile aldehydes, mainly responsible for flavour and odour, are stable under these conditions. For this reason, estimation of the contents of volatile

aldehydes that may be responsible for the rancid odour still perceptible in these fat, has been taken recourse to as an additional measure of oxidative rancidity, with a second set of experiments performed in a sealed tube as before. Lea's bisulphite method (*Ind. Eng. Chem. Anal. Ed.*, 1934 6, 241) has been employed for this purpose and the results are shown in Table IV.

TABLE IV

*Aldehyde value of butterfat stored in limited oxygen supply.*

Expt. No.	Description.	0.002N-I <sub>2</sub> per gram of fat stored after				
		15 days.	30 days	45 days.	60 days.	80 days.
1.	Stored in sealed tube (I)	0	0.10	0.40	1.40	6.60
2.	Control	0	0.05	0.12	0.50	0.85

The results are shown graphically in Fig. 3. The pronounced lag observed in the appearance of aldehyde, as can be seen from the figure, is of interest in view of the ability of the fat to give rise to secondary products of decomposition from the fat peroxide and the Kreis-active substance.

FIG. 3

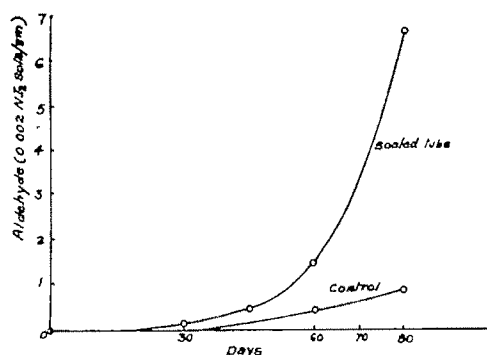
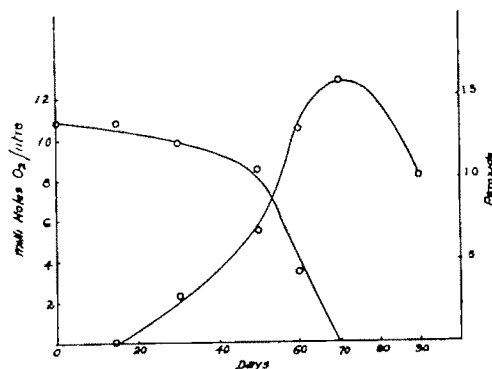


FIG. 4



From the results in Table III it can be said that rancidity can even proceed in a very limited supply of oxygen. It is thus clear that in order to ensure good protection of fat against rancidity one must be sure that the atmosphere should be free from oxygen. Packages in inert gases seems to have good retarding effect on the rate of oxidation, but since rancidity develops even in strictly inert atmospheres, it is of interest to study the effect of small amounts of oxygen that remains dissolved in fat on the development of rancidity of fats. This effect has been studied in the following section.

#### *Dissolved Oxygen and Rancidity*

Development of rancidity slowly proceeds in butterfat even when stored in an inert atmosphere (Table III), though the induction period is very nearly doubled. This points to the fact that in such cases oxidation is brought about by the small amounts of

dissolved oxygen present in the fat itself and so it was considered that estimation of dissolved oxygen during development of rancidity might throw light on this problem.

*Estimation of Dissolved Oxygen in Butterfat.*—There is practically no method of estimating dissolved oxygen in fats and oils in literature. The chemical methods that are prevalent for the estimation of dissolved air in water and sewage, viz. Winkler's and Rideal-Stewart's  $\text{MnSO}_4$  method (*Ber.*, 1888, 21, 2843; *Z. anal. Chem.*, 1914, 53, 665) were found unsuitable for this purpose. Polarographic methods of determining dissolved oxygen in liquids cannot be applied in this case due to the non-conducting and non-ionising nature of oils and fats. Recourse was ultimately taken to manometric methods, using van Slyke's apparatus for the estimation of  $\text{CO}_2$  and combined oxygen in blood, and this proved very advantageous for the present investigation. The method of estimation as given in the Text Book of Practical Physiological Chemistry" by Hawk and Bergeim (9th Ed., pp. 466-67) was adopted with slight changes suitable for the present purpose. The procedure is detailed below.

By means of a differential pipette 2 c.c. of the fat were transferred directly into the extraction chamber by keeping the tip of the pipette immersed to the bottom of the reagent cup, and regulating the admission by finger and stop-cock below the cup. A few drops of mercury were introduced in the cup as a seal after closing the stop-cock. The apparatus was evacuated and shaken for 3 minutes by slowly driving the wheel by hand. Air free 1 N-NaOH (1 c.c.) was placed in the cup and the  $\text{CO}_2$  absorbed by admitting 0.5 c.c. of the hydroxide into the chamber under diminished pressure. The solution meniscus was brought to either 2 c.c. or 0.5 c.c. mark and pressure  $p_1$  (pressure of  $\text{O}_2 + \text{N}_2$ ) was read. The apparatus was brought again under slight negative pressure by means of the levelling bulb and opening the stop-cock below, 0.5 c.c. of hydrosulphite solution (or alkaline pyrogallate solution) was admitted as before by placing 1.0 c.c. of the absorbent in the cup. One drop was admitted at 5 seconds' intervals consuming 2-3 minutes for the entire absorption; the gas was brought to the same mark as before and  $p_2$  (pressure of  $\text{N}_2$ ) was read on the manometer.

$$P_{\text{O}_2} = p_1 - p_2 - c$$

where  $c$  is correction for manometric depression caused by introduction of absorbent solution and can be determined from a separate blank experiment. The result is expressed as

$$\text{millimoles gas/litre} = \frac{P \times \text{vol. \% factor}}{2.24}$$

the volume % factor is given in the table by van Slyke. (*J. Biol. Chem.*, 1921, 49, 30).

Attempts to dissolve the fat in a suitable solvent like pyridine or acetone in order to allow the  $\text{O}_2$  estimation by absorption in a single reaction phase, however, met with little success, as separation of fat always occurred when absorption of oxygen was effected by addition of alkaline pyrogallol or hydrosulphite solution.

For the present experiments, the butterfat was stored at  $37^\circ$  in an incubator<sup>1</sup> in an atmosphere of nitrogen in conical flasks. The flasks provided with inlet and outlet tubes with stop-cock arrangements, were first evacuated by means of a high vacuum

Cenco pump, filled with  $N_2$ , and by repeating this process of evacuation and refilling with  $N_2$ , complete anaerobic conditions were established. Freshly prepared butterfat was carefully poured in a slow stream inside the flasks carefully avoiding formation of bubbles during the transfer, this precaution being necessary to avoid entrapping air. The flasks were kept stored in the incubator at  $37^\circ$ , keeping necessary control. Progress of rancidity was followed by estimation of Kreis and peroxide values and the amount of dissolved oxygen was estimated with several 2 c.c. portions (usually 3 determinations were made), and mean value tabulated. The results are shown in Table V.

TABLE V

A. Butterfat stored in an atmosphere of $N_2$ .							
	Original	After 15 days.	After 30 days.	After 45 days.	After 60 days.	After 70 days.	After 80 days.
1. Millimoles $O_2$ /litre	1.08	1.08	0.98	0.82	0.36	0.0	0.0
2. Millimoles ( $N_2 + CO_2$ )/litre	4.36	4.36	4.10	4.64	4.36	5.0	5.0
3. Total gas (millimoles/litre)	5.44	5.44	5.08	5.46	4.72	5.0	5.0
4. Peroxide value	0	0	0.20	0.67	1.02	1.62	1.05
5. Kreis No.	0	0	1.0	2.1	3.2	3.2	2.0
B. Control sample.							
1. Millimoles $O_2$ /litre	1.08	1.03	1.06	0.95	0.76	0.76	0.64
2. Millimoles ( $N_2 + CO_2$ )/litre	4.4	4.35	4.56	4.56	4.74	4.66	4.65
3. Total gas (millimoles/litre)	5.48	5.43	5.62	5.51	5.50	5.42	5.29
4. Peroxide value	0	0.15	1.0	2.4	3.0	8.0	20.2
5. Kreis No.	0	0.1	1.6	4.2	8.8	10.5	12.0

Estimation of dissolved oxygen during the development of rancidity indicates that increased peroxide formation is accompanied by the an almost proportionate decrease in the amount of dissolved oxygen in the fat. When the whole of oxygen has been used up in peroxide formation, not only further peroxidation is stopped, there is also a subsequent fall in the peroxide content of the fat, due probably to the decomposition of the peroxides already formed. This relationship is clearly shown in Fig. 4, where maximum peroxide formation can be seen to coincide with the minimum oxygen-content (0.0) of the fat.

These experiments along with those performed in a limited oxygen supply go to prove that presence of small amounts of dissolved oxygen is able to produce rancidity in fats, and hence particular care must be taken in ensuring complete removal of this dissolved oxygen when gas packaging is resorted to as a means of preservation of fats from rancidity.



## DISCUSSION

It has been shown that very small amounts of oxygen can produce rancidity of fats and the oxygen that remains dissolved in the oil or fat plays a prominent role in the development of rancidity. The effect of increased oxygen pressure is particularly insignificant in view of the relatively small oxygen requirement of the fats (in developing organoleptic rancidity) and the induction period remains constant throughout ; it is only with pure oxygen that a slight decrease in the induction period has been observed. The decreased oxygen pressure is also without effect on the induction period and here also reduction in the pressure of oxygen fails to cause a proportionate decrease in the rate of onset of rancidity and it is only when the oxygen is completely replaced by  $N_2$ , that an increased induction period can be observed. The experiments with limited oxygen supply lead one to the conclusion that the development of rancidity by peroxide formation proceeds so long as there is available oxygen, and when the latter is used up, there can be observed a fall in the concentration of peroxides and also of the Kreis active component due to decomposition reactions. In such cases, the volatile aldehyde content of the fats may give an indication as to the state of rancidity, Kreis and peroxide values being almost negative at the advanced stage in such cases. Estimation of dissolved oxygen in samples, stored in nitrogen atmosphere, shows a gradual fall in the dissolved oxygen content of the fat as rancidity proceeds and ultimately falls to zero, but one interesting point has emerged from these estimations of dissolved gases in that the total gas (millimoles/litre) is very nearly constant throughout the process, both in the control and test sample.

Rancidity may now be ascribed primarily to the action of dissolved oxygen on the unsaturated constituents of the fats and the rate of development of rancidity may be said to depend on the rate of diffusion of oxygen from the atmosphere to the oil, controlled by the solubility of the gas in the fat or oil concerned.

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DEPARTMENT OF APPLIED CHEMISTRY,  
UNIVERSITY COLLEGE OF SCIENCE  
CALCUTTA.

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## INNER-METALLIC COMPLEX SALTS OF SALICYLALDIMINO-ACIDS WITH POLYCYCLIC RINGS. PART I

BY PRIYADARANJAN RÂY AND AJIT KUMAR MUKHERJEE

A number of complex compounds of bivalent copper, nickel, cobalt and manganese, and of trivalent iron, with salicylaldehyde and amino-acids like anthranilic acid, glycine and alanine have been prepared and their properties studied.

The configuration of these complexes cannot always be represented by unique and unambiguous structural formula. Preference has been given to the most probable of all the possible structures on the basis of their physical properties like solubility, colour and magnetic susceptibilities. The salicylaldehyde molecule in these complexes is believed to undergo condensation with amino-acids giving rise to what may be termed as 'aldimine acids, which can function under suitable conditions as a tridentate molecule in co-ordination complexes. In some cases, they behave as bi-functional molecule with the carboxylic acid group remaining free. The composition and nature of the complexes have been found to depend on the nature of the central metal atom, as also on the nature of the addenda.

Pfeiffer and co-workers (*J. prakt. Chem.*, 1931, **129**, 163; *Annalen*, 1933, **503**, 84; *J. prakt. Chem.*, 1936, **145**, 243; 1938, **151**, 145; 1940, **155**, 77; 1942, **159**, 313; Pfeiffer, *Z. angew. Chem.*, 1940, **53**, 93) in a series of papers have studied the preparation, properties and constitution of a large variety of inner metallic complexes of oxyaldimines and oxyketimines with spiral-like or polycyclic rings. In these, various *o*-oxyaldehydes and diketones were made to condense with monoamines, diamines, and even amides and esters of some amino-acids in presence of metallic salts. They also studied the inner metallic complex salts of salicylaldehyde. A very significant observation was made by the authors in the case of *bis*-salicylaldehyde-cobalt ethylenediamine complex, which turns black from red in air by absorption of oxygen. The absorbed oxygen is again given off by heating the product in CO<sub>2</sub>-atmosphere (Tsumaki, *Bull. Chem. Soc. Japan*, 1938, **12**, 252). This catalytic oxidation has been studied in detail by Calvin and co-workers (*J. Amer. Chem. Soc.*, 1946, **68**, 2254, 2257, 2263, 2267, 2273) in recent years. This interesting chelate complex was synthesised on a large scale and used during the last global war as an effective oxygen carrier or artificial respiratory pigment under the name of *salcomine*. The present work was undertaken with a view to studying similar chelate complexes of copper, nickel, cobalt, manganese and iron with salicylaldehyde and different amino-acids like glycine, alanine, anthranilic acid, etc., as the free amino-acids have not been used by previous workers in the study of this type of chelate complexes. The salicylaldehyde molecule in these complexes is believed to have undergone condensation with amino-acids, which can function as a tridentate molecule under suitable conditions, and sometimes also as a bi-functional ligand with the carboxylic acid group remaining free.

The complex compound of copper salicylaldehyde with anthranilic acid was obtained by the interaction of copper anthranilate and salicylaldehyde in alkaline medium.

It is slightly soluble in water and readily in alcohol and other organic solvents like pyridine, acetone, etc. The anhydrous compound is, however, much less soluble. Copper salicylaldehyde-glycine and -alanine complexes were obtained by the interaction of copper disalicylaldehyde and the aqueous solution of the corresponding amino-acid. Both these compounds are soluble in water, but sparingly soluble in alcohol. They are slightly acidic to litmus. Similar complexes of nickel and cobalt were also prepared; with anthranilic acid nickel, however, gave a sodium salt in presence of caustic soda.

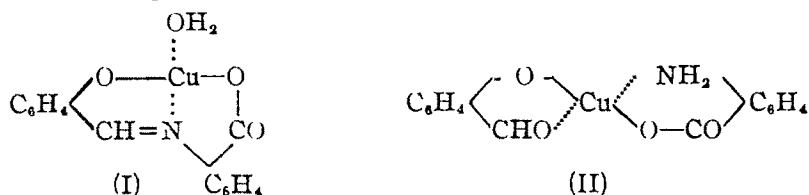
No manganese salicylaldehyde has been described in literature. This was, however, obtained from  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and salicylaldehyde in presence of caustic alkali. The product is readily oxidised by air at the room temperature, and a suspension of the substance in water is markedly blackened by the passage of air. Complexes of manganese salicylaldehyde with glycine and alanine have been prepared, though no corresponding complex with anthranilic acid could be isolated.

Ferrous sulphate, glycine and salicylaldehyde in aqueous alcoholic solution, on being heated for some hours, gave dark red shining crystals of a basic ferric salicylaldehyde-glycine complex, which resembles the corresponding copper and manganese compound in composition.

The constitution of these complexes can be represented as discussed below.

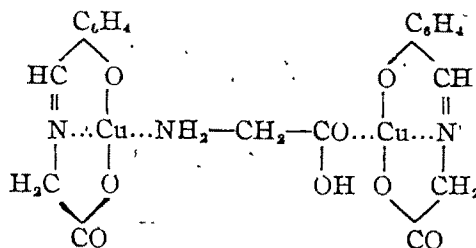
#### Copper Compounds

*Copper-salicylaldehyde-anthranilate.*—Copper combines with a molecule of salicylaldehyde and a molecule of anthranilic acid to form a four-covalent complex which may have the configuration (I), corresponding to that of salicylaldimine compounds and an alternative configuration might have been given by the structure (II):



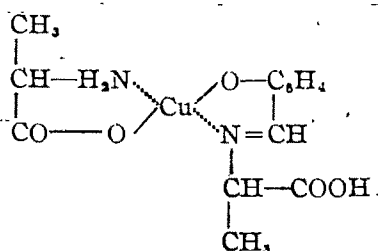
The method of preparation with an excess of salicylaldehyde and the properties of the compound, however, support the structure (I). Its magnetic moment value of 1.79 Bohr differs from those of copper anthranilate ( $1.92\mu_B$ , cf. Rây and Sen, this *Journal*, 1948, **28**, 473) and copper salicylaldehyde ( $1.92\mu_B$ , cf. Tyson and Adams, *J. Amer. Chem. Soc.*, 1940, **62**, 1228). It can therefore be concluded that the copper salicylaldehyde anthranilate is a penetration complex with planar  $dsp^2$  hybrid bonds (Rây and Sen, *loc. cit.*) having the configuration (I). A compound of the configuration (II), which may be viewed practically as an equimolecular mixture of copper salicylaldehyde and copper anthranilate would have possessed a magnetic moment of  $1.92\mu_B$  per copper atom like that of its constituents.

*Copper-salicylaldehyde-glycine.*—The substance is derived from the condensation of two molecules of salicylaldehyde and three molecules of glycine with two atoms of copper. The probable configuration is given by



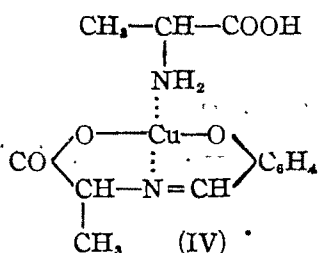
Its magnetic moment value of  $1.82\mu_B$ , and its high solubility in water are in support of the configuration given, in which copper is four-covalent with  $dsp^2$  hybrid planar bonds.

*Copper-salicylaldehyde-alanine.*—This is formed by the condensation of two molecules of alanine and one molecule of salicylaldehyde with one atom of copper. Its configuration is best represented by structure (III).

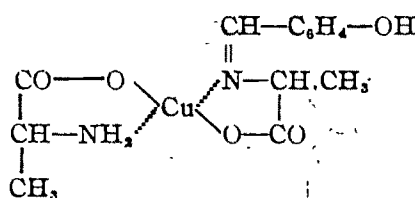


(III)

The structure (IV) is not likely to be stable owing to steric conditions. The properties of the substance, particularly its high solubility in water, also exclude the configuration (V).



(IV)



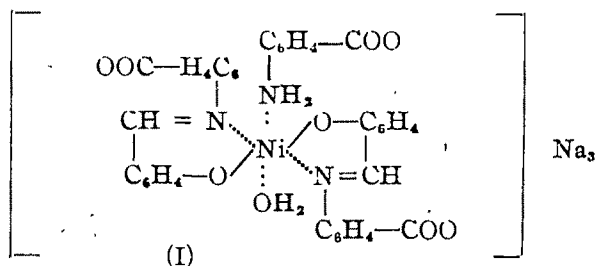
(V)

The moment value of  $1.88\mu_B$  indicates that the copper is possibly present in a planar configuration with hybrid  $dsp^2$  bonds.

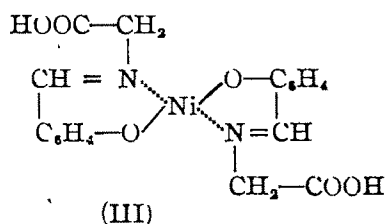
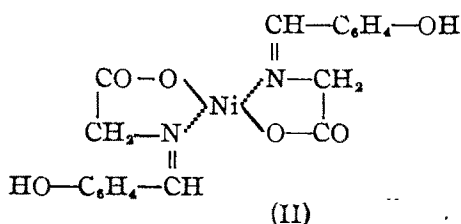
#### Nickel Compounds

All the nickel compounds, described here, show paramagnetic moments of about  $3\mu_B$  corresponding to the presence of two unpaired electrons. This indicates that the bonds in the complex are of the weak co-valent type resonating with ionic ones. They are coloured either green or blue.

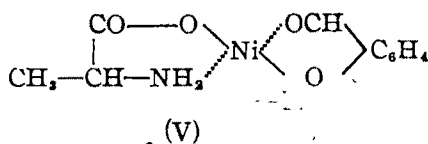
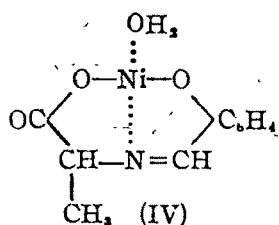
*Sodium-Nickel-salicylaldehyde-anthranilate.*—Two molecules of salicylaldehyde and three molecules of sodium anthranilate condense with a nickel atom to form the complex sodium salt, which can be represented by the octahedral configuration (I).



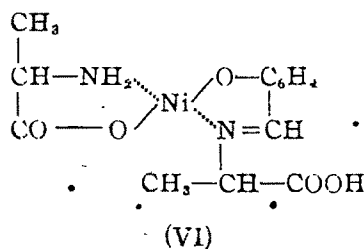
*Nickel-salicylaldehyde-glycine*.—This is formed by the condensation of two molecules of salicylaldehyde and two molecules of glycine with one atom of nickel. As the substance is insoluble in water and slightly soluble in organic solvents, its configuration is best represented by structure (II) in preference to (III).



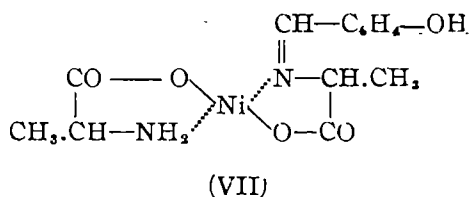
*Nickel-salicylaldehyde-alanine* : (a, green).—One molecule of salicylaldehyde and one molecule of alanine condense with one atom of nickel to give rise to this green complex. As the substance is insoluble in water its configuration is represented by the structure (IV) in preference to (V). The latter may be viewed as a molecular compound of nickel salicylaldehyde and nickel alanine.



*Nickel-salicylaldehyde-alanine* : (b, blue).—This was derived from the condensation of two molecules of alanine and one molecule of salicylaldehyde with one atom of nickel. As the substance is soluble in water and organic solvents, it can be represented by configuration (VI).

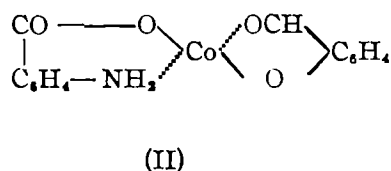
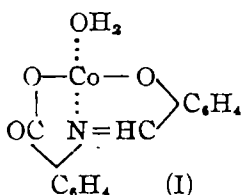


The alternative structure (VII) is thereby excluded.



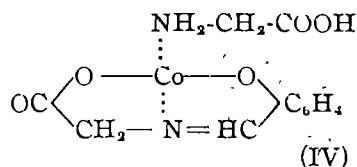
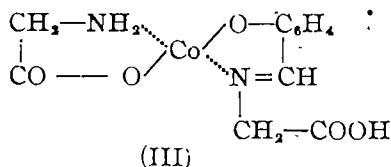
### Cobalt Compounds

*Cobalt-salicylaldehyde-anthranilate.*—This is produced by the condensation of one molecule of anthranilic acid and one molecule of salicylaldehyde with one atom of cobalt. Its intense characteristic colour and the low moment value of  $1.44 \mu_B$  corresponding practically to the spin moment of one unpaired electron, support the configuration (I) for the substance in preference to (II), which latter may be viewed as a molecular compound of cobalt salicylaldehyde and cobalt anthranilate.



The low moment value suggests that the cobaltous atom occurs in a penetration complex with  $dsp^2$  planar bonds.

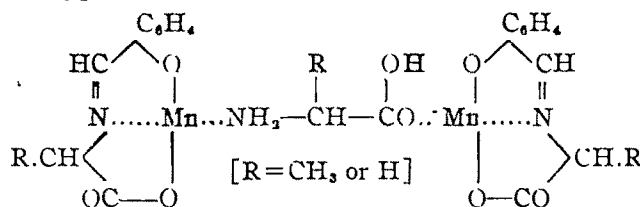
*Cobalt-salicylaldehyde-glycine.*—The compound is formed by the condensation of two molecules of glycine and one molecule of salicylaldehyde with one atom of cobalt. It gives a moment value of  $2.89 \mu_B$ , considerably less than the spin moment of three unpaired electrons usually present in a cobaltous ion. The substance is also soluble in water and possesses a characteristic deep brown colour. It may therefore be regarded as a penetration complex with planar  $dsp^2$  bonds of the configuration (III) in preference to (IV) for steric consideration.



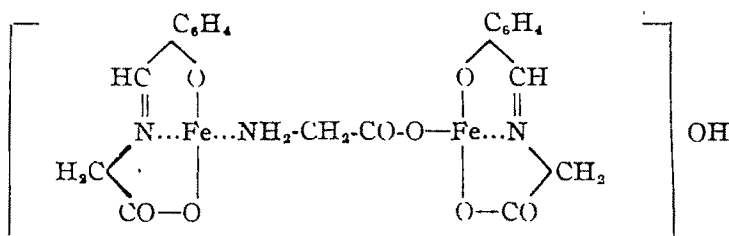
*Cobalt-salicylaldehyde-alanine.*—It resembles the corresponding green nickel alanine compound, being derived from the condensation of one molecule of alanine and one molecule of salicylaldehyde with one atom of cobalt. It gives a moment value of  $4.59 \mu_B$ , agreeing approximately with that for cobaltous ion. Hence, the bonds in the complex are likely to be of the weak co-valent type resonating with ionic ones. It should therefore be represented by a configuration similar to that of the green nickel alanine complex. The structure is also similar to that of the cobalt salicylaldehyde anthranilate, though the nature of the bond differs in the two.

*Manganese Compounds*

Both glycine and alanine give the same type of compounds with manganese and salicylaldehyde resembling the copper-glycine-salicylaldehyde in composition. These are therefore represented by the configuration given below. Both the compounds give a moment value of  $6\mu_B$  approximately, corresponding with that of manganous ion. Hence, the metal atom in the complex forms weak co-valent bonds resonating with those of the ionic type.

*Iron Compounds.*

*Iron-salicylaldehyde-glycine (ferric).*—This is produced by the condensation of three molecules of glycine and two molecules of salicylaldehyde with two atoms of iron. Its composition and structure resembles more or less those of the corresponding copper and manganese compounds with some difference due to the tervalency of the metal atom.



The magnetic moment value of  $5.91 \mu_B$  indicates that the iron is in the ferric state and the bonds are of the weak  $sp^3d$  type resonating with those of the ionic one.

From a comparison of the composition and the structure of the various compounds it will be noticed that the nature of the compound often varies with the nature of the central metal atom involved in its formation. Thus, though the sparingly soluble copper and cobalt salicylaldehyde anthranilate possess similar composition and are non-electrolyte in character, the corresponding nickel compound differs from them and gives rise to a soluble sodium salt.

With glycine and salicylaldehyde, copper, nickel and cobalt, all give compounds of different composition. With alanine and salicylaldehyde nickel gives two types of compounds, one of which resembles the corresponding copper compound, and the other, the corresponding cobalt compound.

Manganese with glycine or alanine and salicylaldehyde gives compounds which resemble the copper-salicylaldehyde-glycine in composition and physical properties.

Iron, though used in the form of a ferrous salt, condenses with salicylaldehyde and glycine to give a complex basic ferric compound.

## E X P E R I M E N T A L

*Copper-salicylaldehyde-anthranilate.*—About 2 g. of pure copper acetate was dissolved in the minimum quantity of water with the addition of 1 to 2 drops of glacial acetic acid. A solution of 2.72 g. of pure, recrystallised anthranilic acid in rectified spirit was added to the copper solution. Light green copper anthranilate was precipitated. The product was filtered, washed first with water, then with alcohol, and finally dried in air. The copper anthranilate was then suspended in alcohol and treated with 2.5 g. of pure salicylaldehyde. The resulting mixture was warmed on the water-bath and treated with less than its equivalent quantity of pure NaOH solution (0.64 g.), when a clear green solution was obtained. This was filtered hot and the filtrate, on standing, gave fine greenish blue crystals. These were filtered and recrystallised from alcohol. The crystals were dried in air. [Found: Cu, 18.23; N, 4.06; salicylaldehyde, 35.50;  $H_2O$  (by loss at  $110^\circ$ ), 11.68.  $Cu(C_{14}H_9NO_3)_2 \cdot 2.5H_2O$  requires Cu, 18.26; N, 4.04; salicylaldehyde, 35.35;  $H_2O$ , 12.94 per cent].

[Found (dried at  $110^\circ$ ): Cu, 20.66; N, 4.52. Calc. Cu, 21.01; N, 4.64 per cent]. Only a part of the water is removed by drying.

Copper was estimated volumetrically after decomposition of the substance with  $H_2SO_4$  (conc.) and a little  $HNO_3$  (conc.). Nitrogen was estimated as usual by the Kjeldahl process after decomposition of the substance with concentrated  $H_2SO_4$ , with the addition of potassium sulphate and copper sulphate. Salicylaldehyde was estimated as copper salicylaldoxime, as described below.

To a known amount of the substance, 90. c.c. of a buffer solution (50. c.c. glacial acetic acid and 10 g. sodium acetate dissolved in 450. c.c. of water) was added, followed by 10 c.c. of 1% copper acetate solution. The mixture was stirred well and treated with a concentrated solution of 0.2 to 0.5 g. of hydroxylamine hydrochloride. The mixture was heated on the water-bath at  $80^\circ$ . The greenish yellow precipitate of copper salicylaldoxime was then filtered through a Gooch crucible, washed with hot water, and dried at  $110^\circ$ .

Copper salicylaldehyde anthranilate forms fine greenish blue crystals, slightly soluble in water, but readily in alcohol, pyridine and acetone. The solution of the substance is almost neutral to litmus and is decomposed by acids. It decomposes, on heating to about  $120^\circ$ , with separation of salicylaldehyde.

*Copper-salicylaldehyde-glycine.*—About 1.5 g. of pure copper salicylaldehyde was added to a solution of 2 g. of glycine in a little water. The mixture was shaken vigorously and warmed on the water-bath, and then filtered while hot. The filtrate, on standing, deposited shining blue needle-shaped crystals. These were washed first with water and then with alcohol. The product was recrystallised from water and dried in air. [Found: Cu, 22.58; N, 7.43; salicylaldehyde, 42.70;  $H_2O$  (by loss at  $110^\circ$ ), 0.98.  $Cu_2(C_{20}H_{19}N_3O_8) \cdot 0.5H_2O$  requires Cu, 22.51; N, 7.45; salicylaldehyde, 43.24;  $H_2O$ , 1.60 per cent].

Thus only a part of the water is removed by drying at  $110^\circ$ .



The substance forms blue shining crystals, readily soluble in water, but practically insoluble in alcohol, acetone and chloroform. Its aqueous solution reacts acidic to litmus. It is decomposed by acids, but unaffected by alkalies.

*Copper-salicylaldehyde-alanine*.—About 2 g. of copper salicylaldehyde in alcoholic suspension was treated with an aqueous solution of 1.75 g. of alanine. The mixture was warmed on the water-bath, when a clear green solution was obtained. This was filtered. From the filtrate, on standing, shining crystals separated gradually. The crystals were first washed with water, then with alcohol and finally dried in air. [Found: Cu, 18.47; N, 8.20; salicylaldehyde, 35.05.  $\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_3)$  requires Cu, 18.49; N, 8.14; salicylaldehyde, 35.50 per cent].

The substance forms blue shining crystals, readily soluble in water, but sparingly soluble in acetone, chloroform and benzene and moderately in pyridine. Its aqueous solution reacts slightly acidic to litmus. It is decomposed by dilute mineral acids, but is unaffected by alkalies.

*Nickel-salicylaldehyde-glycine*.—About 3 g. of freshly prepared nickel salicylaldehyde in alcoholic suspension was treated with a solution of glycine (4 g.) in water. The mixture was warmed on the water-bath and filtered hot. The filtrate, on standing overnight, gave a crop of blue-violet crystals. These were washed first with cold water and then with alcohol, and finally dried in air. [Found: Ni, 14.07; N, 6.80; salicylaldehyde, 57.33.  $\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_4)$  requires Ni, 14.13; N, 6.74; salicylaldehyde, 58.83 per cent].

The substance forms blue-violet crystals, insoluble in water, alcohol and acetone, but very slightly soluble in pyridine. It is decomposed by mineral acids and strong alkalies, as also by boiling with water.

Nickel was estimated as nickel dimethylglyoxime after decomposition of the substance with concentrated  $\text{H}_2\text{SO}_4$  and a little concentrated  $\text{HNO}_3$ . Salicylaldehyde was estimated as copper salicylaldehyde as before.

*Nickel-salicylaldehyde-alanine (green)*.—Freshly prepared nickel salicylaldehyde (4 g.) was treated in aqueous suspension with a solution of alanine (2.4 g.) in water. The resulting mixture was warmed on the water-bath. The insoluble product was filtered, washed first with water, then with rectified spirit, and finally dried in air. [Found: Ni, 22.35; N, 5.51; salicylaldehyde, 45.26;  $\text{H}_2\text{O}$  (by loss at  $110^\circ$ ), 6.18.  $\text{Ni}(\text{C}_{10}\text{H}_7\text{NO}_3)$ ,  $\text{H}_2\text{O}$  requires Ni, 21.92; N, 5.22; salicylaldehyde, 45.56;  $\text{H}_2\text{O}$ , 6.72 per cent]. Only a part of the water is removed by drying at  $110^\circ$ .

The substance forms shining green crystals, insoluble in cold water, but slightly soluble in warm water. It is sparingly soluble in alcohol, but readily in pyridine and acetone. Mineral acids and strong alkalies decompose it.

*Nickel-salicylaldehyde-alanine (blue)*.—Nickel salicylaldehyde (4 g.) in alcoholic solution was treated with solid alanine (3.75 g.) and warmed on the water-bath, when a bluish green solution was obtained. The solution was filtered while hot and the filtrate, on standing, gave fine light blue shining crystals, different from that obtained in the previous operation. The crystals were washed first with a little water, then with alcohol, and finally dried in air. The filtrate, on standing, gave a crop of shining light green crystals of the previous compound. [Found: Ni, 16.02; N, 7.63;

salicylaldehyde, 33.16.  $\text{Ni}(\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_8)$ ,  $1.5\text{H}_2\text{O}$  requires Ni, 16.04; N, 7.66; salicylaldehyde, 33.46 per cent]. The substance loses only a part of its water at  $110^\circ$ .

*Nickel-salicylaldehyde-anthranilate (Na-salt).*—Nickel anthranilate, prepared from 4 g. of nickel acetate and anthranilic acid, was suspended in alcohol and treated with 2.95 g. of salicylaldehyde. The resulting mixture was warmed on the water-bath and treated with a slight excess of caustic soda. The solution was filtered while hot. The filtrate, on standing, deposited silky yellow crystals, which were recrystallised from alcohol. {Found: Ni, 7.76; N, 5.64; salicylaldehyde, 31.06; Na, 9.06.  $[\text{Ni}(\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_8)] \text{Na}_2, \text{H}_2\text{O}$  requires Ni, 7.74; N, 5.52; salicylaldehyde, 32.13; Na, 9.08 per cent}. The substance loses only a part of its water at  $110^\circ$ .

It forms silky yellow crystals, sparingly soluble in water, but fairly soluble in alcohol and acetone. Its solution is alkaline to litmus. The substance is decomposed by mineral acids.

*Cobalt-salicylaldehyde-glycine*—About 4 g. of glycine, dissolved in a little water, was mixed with 3 g. of freshly prepared cobalt salicylaldehyde. The resulting mixture was thoroughly shaken, warmed on the water-bath, and then filtered while hot. The filtrate, on standing, gave violet-brown silky needles. These were washed first with water, then with alcohol, and finally dried in air. [Found: Co, 18.38; N, 8.72; salicylaldehyde, 38.24;  $\text{H}_2\text{O}$  (by loss at  $110^\circ$ ), 2.49.  $\text{Co}(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_8)$ ,  $0.5\text{H}_2\text{O}$  requires Co, 18.40; N, 8.75; salicylaldehyde, 38.72;  $\text{H}_2\text{O}$ , 2.81 per cent].

The substance is soluble in water, but insoluble in alcohol and slightly soluble in pyridine and dioxane. Its aqueous solution reacts somewhat acidic to litmus. It is decomposed by mineral acids and strong alkalis.

*Cobalt-salicylaldehyde-alanine.*—Freshly prepared cobalt salicylaldehyde (3 g.) in alcoholic suspension was treated with alanine (2 g.) dissolved in a little water. The mixture was warmed on the water-bath, when the colour of the product changed to brick-red. This was then filtered, washed and dried as before. [Found: Co, 21.84; N, 5.35; salicylaldehyde, 45.44;  $\text{H}_2\text{O}$  (by loss at  $110^\circ$ ), 6.14.  $\text{Co}(\text{C}_{10}\text{H}_9\text{NO}_3)$ ,  $\text{H}_2\text{O}$  requires Co, 22.01; N, 5.23; salicylaldehyde, 45.52;  $\text{H}_2\text{O}$ , 6.70 per cent]. The water therefore could not be completely removed by drying at  $110^\circ$ .

The substance forms brick-red crystals, insoluble in water, but slightly soluble in pyridine and acetone. It reacts neutral to litmus, and is decomposed by dilute mineral acids and strong alkalis.

*Cobalt-salicylaldehyde Anthranilate.*—Cobalt acetate (4 g.), dissolved in the minimum amount of water with the addition of 2 to 3 drops of glacial acetic acid, was treated with an alcoholic solution of pure anthranilic acid (4.45 g.). The precipitate of cobalt anthranilate, after being washed and dried, was suspended in alcohol and treated with salicylaldehyde (3.85 g.). The mixture was then warmed on the water-bath and treated with a solution of caustic soda (0.85 g. dissolved in a little water). The mixture was afterwards filtered while hot. On standing, brown needle-shaped silky crystals separated from the filtrate. These were recrystallised from alcohol and finally dried in air. [Found: Co, 18.57; N, 4.47; salicylaldehyde, 37.66;  $\text{H}_2\text{O}$  (by loss at  $110^\circ$ ), 4.89.  $\text{Co}(\text{C}_{14}\text{H}_9\text{NO}_8)$ ,  $\text{H}_2\text{O}$  requires Co, 18.67; N, 4.43; salicylaldehyde, 38.62;  $\text{H}_2\text{O}$ , 5.71 per cent]. This indicates that only a part of the water was lost by drying at  $110^\circ$ .

The substance forms yellowish brown silky needles, sparingly soluble in water, but more soluble in alcohol and other organic solvents. When crystallised from pyridine it gave shining yellow scales which were found to contain pyridine. Its solution reacts almost neutral to litmus, and it is decomposed by mineral acids and strong alkalies.

Cobalt was estimated as  $\text{CoSO}_4$  after decomposition of the substance with concentrated  $\text{H}_2\text{SO}_4$ . Nitrogen and salicylaldehyde were estimated as before.

*Manganese-salicylaldehyde*.—About 3 g. of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and 4 g. of salicylaldehyde were mixed together in a conical flask, and the mixture was treated dropwise with a solution of caustic soda (0.4 g.). The yellow precipitate formed, was filtered, washed first with water, then with alcohol, and afterwards dried in air. The substance blackens slowly on exposure to air. [Found: Mn, 16.68; salicylaldehyde, 67.92.  $\text{Mn}(\text{O}_2\text{C}_6\text{H}_4\text{CHO})_2 \cdot 2\text{H}_2\text{O}$  requires Mn, 16.51; salicylaldehyde, 73.27 per cent].

The results show that the substance could not be obtained in a pure state.

The substance is sparingly soluble in water and alcohol, but readily in pyridine. It turns black on passing air through its aqueous suspension. The substance is decomposed by mineral acids.

*Manganese-salicylaldehyde-glycine*.—About 3 g. of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , dissolved in a little water, was treated with 4 g. of salicylaldehyde, followed by an excess of sodium acetate. About 2.45 g. of glycine was then added to the resulting yellow solution. A light yellow precipitate was obtained which was washed and dried as usual. [Found: Mn, 20.07; N, 7.56; salicylaldehyde, 44.25.  $\text{Mn}_2(\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_8) \cdot 0.5\text{H}_2\text{O}$  requires Mn, 20.07; N, 7.35; salicylaldehyde, 44.64 per cent].

The substance is insoluble in water and many organic solvents but soluble in pyridine and dioxane. It reacts slightly acidic to litmus. Dilute mineral acids, or acetic acid, and strong alkalies lead to its decomposition.

*Manganese-salicylaldehyde-alanine*.—Freshly prepared crude manganese salicylaldehyde (3 g.) in alcoholic suspension was treated with alanine (2.5 g.), dissolved in a little water. The mixture was warmed on the water-bath and the insoluble product was filtered. This was washed and dried as usual. [Found: Mn, 18.80; N, 7.03; salicylaldehyde, 41.88.  $\text{Mn}_2(\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_8) \cdot 0.5\text{H}_2\text{O}$  requires Mn, 18.65; N, 7.12; salicylaldehyde, 41.66 per cent].

The substance forms yellow crystals, slightly soluble in water and alcohol, but readily in pyridine, acetone and dioxane. It reacts slightly acidic to litmus, and is decomposed by dilute mineral acids and strong alkalies.

Manganese was estimated gravimetrically as  $\text{MnSO}_4$  after the ignition of the substance, followed by a treatment with  $\text{HCl}$  (conc.) and  $\text{H}_2\text{SO}_4$  (conc.). Nitrogen and salicylaldehyde were estimated as in the previous cases.

*Iron-salicylaldehyde-glycine (Ferric)*.—Freshly recrystallised  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , dissolved in a little water, was treated with glycine (1 g.), followed by the addition of an alcoholic solution of salicylaldehyde (1.75 g.). The resulting deep red solution was refluxed on the water-bath for about two hours. Dark red shining crystals gradually separated from the solution. The mixture was kept overnight in the cold. The crystals were then filtered, washed and dried as usual. A further crop was obtained from the mother-liquor by the addition of sodium acetate. [Found: Fe, 18.87; N, 7.02; sali-

cylaldehyde, 40.82.  $[\text{Fe}_2(\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}_8)] \text{OH}, 2\text{H}_2\text{O}$  requires Fe, 1.88; N, 7.08; salicylaldehyde, 41.14 per cent}.

The substance forms dark red shining crystals, soluble in water and alcohol, but readily in pyridine and methoxy-ethanol. It is, however, insoluble in acetone, dioxane, ether and other organic solvents. It reacts neutral to litmus, and is decomposed by dilute mineral acids and strong alkalies. It also decomposes in solution when heated. An acidified solution of the substance becomes colorless, but gives a blood-red coloration with potassium thiocyanate, indicating that the iron is present in the ferric state. This is also supported by magnetic measurement.

Iron was estimated volumetrically after decomposition of the substance with concentrated  $\text{H}_2\text{SO}_4$ . Nitrogen and salicylaldehyde were estimated as before.

#### Magnetic Measurements

The magnetic susceptibilities of the substances were measured in a Gouy's balance with a field strength of  $9.36 \times 10^3$  gauss, taking all the necessary precautions, as described in the previous papers. The results of measurements at  $32^\circ$  are tabulated below.

Name of the substance.	$\chi_g \times 10^6$ .	$\chi_M \times 10^6$ .	$\delta \times 10^6$ .	$\chi_M \times 10^6$ (corr.)	$\mu_B$ (effective)
1. Copper-salicylaldehyde-anthranilate (green)	3.37	1172	-133.9	1306	1.79
2. Copper-salicylaldehyde-glycine (greenish blue)	4.49	2524	-201.0	2725	1.82
3. Copper-salicylaldehyde-alanine (blue)	3.81	1305	-149.0	1454	1.88
4. Nickel-salicylaldehyde-glycine (pale blue-violet)	9.01	3736	-175.7	3911	3.09
5. Nickel-salicylaldehyde-alanine (green)	14.59	3908	-108.0	4015	3.14
Nickel-salicylaldehyde-alanine (light blue)	8.06	2947	-166.0	3113	2.76
7. Nickel-salicylaldehyde-anthranilate (sodium) (greenish yellow)	6.07	4612	-352.6	4965	3.47
8. Cobalt-salicylaldehyde (orange-yellow)	25.15	8017	-144.4	8161	4.46
9. Cobalt-salicylaldehyde-glycine (brown-violet)	10.30	3296	-130.0	3426	4.50(T&A) 2.89
10. Cobalt-salicylaldehyde-alanine (brick-red)	32.70	8489	-108.0	8597	4.59
11. Cobalt-salicylaldehyde-anthranilate (yellowish brown)	2.26	712.9	-134.0	847	1.44
12. Manganese-salicylaldehyde-glycine (yellow)	50.30	27564	-216.6	27781	5.84
13. Manganese-salicylaldehyde-alanine (yellow)	50.30	30740	-261.0	31001	6.15
14. Iron-salicylaldehyde-glycine (dark red)	47.40	28250	-105.0	28355	5.91

$\delta$  = diamagnetic correction. T & A = Tyson and Adams, *loc. cit.*

The authors' best thanks are due to Mr. N. N. Ghosh, M.Sc., for his ungrudging assistance during the course of the work.

INORGANIC CHEMISTRY LABORATORY,  
UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA.

Received June 3, 1950.

## REVIEWS

**Annual Reports on the Progress of Chemistry for 1949—issued by the Chemical Society London.**—The reports for 1949, as usual, have been divided into six chapters. I. General and Physical Chemistry, II. Crystallography, III. Inorganic Chemistry, IV. Organic Chemistry, V. Biochemistry, and VI. Analytical Chemistry. Under I, there are twelve sub-sections which, barring sections 11 and 12, deal mainly with publications between Aug. 1948 and July 1949. Section 11 on magneto-chemistry and section 12 on Metals and alloys claim to represent self-contained treatment of the respective subjects covering a wider period including that of the war. But the report on magneto-chemistry in which the present reviewer is somewhat interested seems to be far from satisfactory and comprehensive. No reference has at all been made to the magnetochemical studies of many interesting compounds including those of tervalent copper, trivalent silver and quadrivalent nickel by the Italian and Indian workers. (Rây *et al.*, *J. Indian Chem. Soc.*, 1948, **28**, 51; Rây & Sarma, *Nature*, 1946, 927; Rây and Sahu, *J. Indian Chem. Soc.*, 1946, **23**, 161; Malatesta, *Gazzetta*, 1941, **71**, 467, 580; Rây and Chakrabarty, *J. Indian Chem. Soc.*, 1944, **21**, 47; Rây and Sen, *ibid*, 1948, **26**, 473).

The chapters on crystallography gives a report on works carried out during 1947, 1948 and 1949, arranged under structure analysis and crystal chemistry.

The Report on Inorganic Chemistry appears to be quite satisfactory excepting the portion under Group VIII, dealing particularly with the co-ordination complexes.

Under Organic Chemistry, essay articles on some important topics like, "Long Chain aliphatic compounds", "Vitamin A and related Polyenes", "Amino-acids", "Alkaloids", "Proteins", and certain aspects of "theoretical Organic Chemistry", which were not fully reviewed in previous years, have been introduced.

The Chapter on Biochemistry records the notable advances made in the various fields of the subject during the year.

The Chapter on Analytical Chemistry presents accounts of certain discrete topics, namely, organic and gravimetric analysis; application of Raman Spectra for analytical purpose, use of organic reagents, gas analysis and radioactivation analysis.

The volume under review will undoubtedly be a valuable addition to all research libraries.

P. Rây.

**Festskrift Tillägnad J. Arvid Hedvall. Göteborg, 1948.**—This is a festival publication in celebration of the eminent Swedish Chemist, Professor Arvid Hedvall's sixtieth birthday. The publication has been enriched with a great variety of articles, contributed by many distinguished scientists of different countries, dealing with multifarious topics and problems of chemistry and physics. Like the contributors, the languages of the contribution are also varied which comprise English, German and Swedish. As the articles are contributed by the specialists in their respective subjects, they are sure to be of great interest and value to all advanced students and workers in chemistry.

P. Rây.

*Annual Report*

ANNUAL REPORT  
OF THE  
INDIAN CHEMICAL SOCIETY  
FOR 1950

## ANNUAL REPORT FOR THE YEAR 1950

The Society is proud of its achievements during the last twenty-six years and it has continued to play an increasingly important role in the furtherance of chemical researches in India. The Society is gaining in strength from year to year by the enrolment of a large number of Fellows and by the receipts of donations and grants from the States, the Universities and the Industrial concerns ; we hope that the Society will prove its usefulness more and more with the active co-operation of its Fellows and Subscribers.

It is highly encouraging to note that the Society has to meet the continuous demand of the back volumes of the Journal by Universities and Libraries from all parts of the world and unless the Society reprints the back issues of the Journals immediately, it will not be able to supply the back numbers. The Society has, however, been faced with the problem of increasing the bulk of the Journal to accommodate the research papers which have been steadily increasing.

In order to maintain a healthy efficiency in the general administration of the affairs of the Society and to cope with the volume of the work the services of a whole-time Assistant Secretary, instead of a part-time one, have been found to be indispensable, and an Assistant Secretary has been appointed temporarily since May 1950. It should be pointed out in this connection that as soon as funds are available a better grade of salary should be recommended for an Assistant Secretary.

The Society is in urgent need of a trained staff for the efficient maintenance of the library. The Society has applied to the Government of India for a recurring grant for the development and maintenance of the Library in view of the fact that the Society possesses valuable chemical Journals from all over the world which are utilised by the Fellows for reference.

At the invitation of the President, 75th Anniversary Celebrations of the American Chemical Society to be held in September, 1951, in New York, Dr. N. R. Dhar has been nominated as the official delegate of our Society. The Society sent its good wishes to the National Congress of Pure and Applied Chemistry held at Milan in September, 1950.

Prof. P. Ray and Dr. B. B. Dey have been nominated as representatives of the Society to the Symposium on the History of Chemistry in South Asia, sponsored by the Department of Scientific Research, Government of India, New Delhi.

The Society has been represented by Dr. U. P. Basu and Mr. S. P. Sen on the Drugs Technical Advisory Board.

## PUBLICATION OF THE JOURNALS

The Hony. Secretary is glad to report that it has been possible to maintain the regularity in the publication of the Journals by tiding over many difficulties, financial and otherwise. Twelve issues (Dec., 1949 to Nov, 1950) of the main Journal and three issues of the Industrial and News Edition (Nos. 3 & 4 of 1949, No 1 and Nos. 2 & 3 of 1950) have been published during the year under review. 132 papers (as against 115 of 1949) have been printed covering 684 pages (as against 590 of 1949) of the main Journal, and 41 papers (as

against 9 of 1949) have been printed covering 308 pages (as against 126 of 1949) of the Industrial & News Edition. In spite of this increase in the number of papers published during the year it has not been possible to publish all the papers communicated during this period. In order to avoid unnecessary delay in the publication of papers it is absolutely necessary to increase the volume of the Journal and allot more money towards publication expenses.

The grateful thanks of the Society are due to the University of Calcutta for printing free of cost 528 pages (excluding cover and advertisement pages) of the main Journal. As the Journal of the Indian Chemical Society is in increasing demand year after year the University of Calcutta has kindly agreed during the year under review at the request of the Society to print 1500 copies (instead of 1000 copies) of 1000 pages free of cost.

In order to ensure regularity in publication the Society had to take the help of other presses in printing 4 issues of the main Journal (covering 188 pages) at a printing cost of Rs. 1,650/-, 3 issues of the Industrial and News Edition (covering 308 pages) at a printing cost of Rs. 2,500/-, and Index (main Journal, 1948) at a cost of Rs. 140/-. The Society had also to employ one compositor (working at the Calcutta University Press) on a pay of Rs. 1080/- per annum.

#### PAPERS COMMUNICATED AND PUBLISHED

During the current year 200 scientific communications including short notes (as against 147 of 1949) have been communicated to the Society for publication in its main Journal. Out of the 200 papers (and notes), 50 papers have been accepted with editorial revision and 63 papers after modification by authors; 6 papers have been transferred to the Industrial & News Edition, and 1 paper was withdrawn. 52 papers (as against 21 of 1949) are awaiting publication in the forthcoming issues of the Journal; the rest are in circulation with authors, Associate Editors and referees. The list of papers communicated during the year have been published along with the notices of the Ordinary General meetings.

During the year under review the Society has received 35 papers (as against 23 of 1949) for publication in the Industrial & News Edition excluding 6 papers transferred from the main Journal. Out of these 41 papers, 9 have been published during the year, and 14 papers are awaiting publication in the future issues and the rest are in circulation.

9 papers received for the Symposium (held in connection with the Silver Jubilee Celebrations) have been published during the year.

#### ORGANISATION OF THE LIBRARY

At present the Society possesses 2294 copies of bound volumes (as against 2197) mainly received in exchange. During the year under review 97 bound volumes of Journals have been added to the Library. Five new exchange relationships have been established. Requests for re-establishment of exchange relationship existing before the war are being received, and many foreign Universities, Societies and Libraries are frequently applying to receive our Journals in exchange of their publications.

The Society has purchased during the year under review 50 worth of Book Coupons (UNESCO), through the Ministry of Education, Govt. of India.



## **PUBLICATION OF HISTORY OF CHEMISTRY IN ANCIENT & MEDIÆVAL INDIA**

During the year under review much progress has been made in the preparation of the manuscripts of "History of Hindu Chemistry". The following chapters have been compiled :

- (1) History of chemistry of the Indus Valley civilisation, including the history of copper and copper-alloy metallurgy.
- (2) History of copper, copper-alloy and iron metallurgy with examination of archaeological specimens from the Vedic period to 500 A. D.
- (3) The chemical arts and crafts of this period other than metallurgy.

## **ACHARYA P. C. RAY MEMORIAL FUND**

Donations received this year towards Acharya P. C. Ray Memorial Fund are Rs. 7,319/- plus Rs. 1,256/- (as interest) only. The total amount collected so far is Rs. 52,190/14/- only. The amount spent under this head is Rs. 1,137/15/- only. Inspite of the issue of a large number of appeals to our Fellows, Industrial firms and Associations the response has not been at all up to expectations. It has, therefore, not been possible to give effect to the two important original intentions of the Memorial Committee, viz., to grant scholarships to meritorious post-graduate students of chemistry all over India, and to award the Annual P. C. Ray Memorial prize to the best Indian research worker working in India. The Government of West Bengal has very kindly promised to make a contribution of 25% of the total collection of Rs. 2 lakhs, provided that the balance of 75% is raised by us from other sources. The West Bengal Government has also agreed to the grant of Rs. 25,000/- as soon as we can raise a fund of Rs. 75,000/-. We have requested the West Bengal Government to grant a proportionate amount of the fund already raised. There can be no difference of opinion about the desirability of giving awards to facilitate research in India, and associating the name of Acharya Prafulla Chandra Ray with such awards and prizes. The Society appeals to the Fellows to collect donations to this fund so that the target amount of Rs. 2 lakhs may be raised in a short time.

## **ACHARYA P. C. RAY MEMORIAL LECTURE**

The third Acharya P. C. Ray Memorial Lecture was delivered by Dr. J. C. Ghosh on 2nd August, 1950. The Lecturer gave an account of his reminiscences of his revered Guru and dwelt in his address on the scope and value of the work of Acharya P. C. Ray, the scientist, the research worker and the teacher.

### DONATIONS

The Council record with grateful thanks the receipt of the following donations to the general funds of the Society for publication :

Govt. of India (recurring, for 1949)	...	...	...	Rs. 3,000/-
National Institute of Sciences of India	...	...	...	500/-
Govt. of West Bengal (non-recurring)	...	...	...	3,000/-
Bengal Chemical & Pharmaceutical Works Ltd., Calcutta	...	...	...	500/-
Osmania University (including Rs. 100/- due last year)	---	---	---	200/-
University of Bombay	...	...	...	300/-
Indian Institute of Science, Bangalore	...	...	...	Rs. 150/-
Calcutta Chemical Co., Calcutta (due last year)	...	...	...	500/-
(in a monthly instalment of Rs. 100/- from September, 1950)	...	...	...	200/-

### FELLOWS AND ASSOCIATE MEMBERS

During the year under review 81 new Fellows have been admitted (vide Appendix B, as against 113 in 1949) and 13 former fellows have been re-instated. 11 Fellows have formally resigned (against 3 in 1949), and the number of Fellows deceased is 2.

89 Fellows in 1949 and 80 Fellows in 1948 were in arrears. Dues for 1949 have been realised from 58 Fellows, and subscriptions from 114 Fellows are in arrears for 1950, and from 31 Fellows for 1949.

During the year the following Life-members have been enrolled : (1) Dr. R. C. Kapoor, D. Phil., Lecturer in Chemistry, Allahabad University, Allahabad, (2) Dr. M. A. Saboor, M. Sc., Ph. D., A.R.I.C., Deputy Director of Industries, West Bengal, (3) Dr. B. Chatterjee, D. Sc., Professor of Chemistry, Shibpur Engineering College, Howrah, bringing the total number of Life-members to 36.

The total numerical strength of Fellows (up to December 15, 1950) stands at 549 (against 498 in 1949). The total number of Associate Members during 1950 is 42 (against 26 in 1949) of whom 34 have been elected this year.

The Council records with deep sense of sorrow the loss sustained by the Society at the death of Dr. P. Neogi who was a Foundation Fellow of the Society, Honorary Treasurer and a Member of the Council for a number of years, and of Dr. D. N. Chakravarti, Calcutta, who was a Fellow of the Society (1931—1950).

### SUBSCRIBERS

During the current year 43 new subscriptions have been recorded, while 75 subscribers have discontinued, of whom 12 subscribers of Pakistan could not pay their subscriptions on account of difficulties attending remittances. The total number of subscribers (up to December 15, 1950) is 286 (as against 318 in 1949), of which 97 are composite subscribers.

### EXCHANGE OF PUBLICATIONS

During the year under review journals have been received in exchange, a complete list of which is published in Appendix A.

### REVIEWS

The following books have been reviewed in the main Journal and Industrial & News Edition.

1. Die Thermodynamik des Wärme—Und Stoffaustausches in der Verfahrenstechnik—By Dr. Ing. Werner Matz.
2. High Polymer Physics : A Symposium—By Howard A. Robinson.
3. Gmelins Handbuch der Anorganischen Chemie—8 Auflage, System Number 18, Antimon. Teil B. 2.
4. Modern Plastics (2nd. Ed., revised & enlarged)—By Harry Barron.
5. Chyma : Annual Studies in the History of Chemistry, Vol. II—By Tenny L. Davis.
6. Quarterly Reviews, Vol. II, No. 1, 1948, The Chemical Society, London.
7. Frontiers in Chemistry, Vol. 8, Frontiers in Colloid Chemistry—Edited By R. E. Burk and Oliver Grummitt.
8. Electron Microscopy—By Ralph W. G. Wyckoff.
9. Technique of Organic Chemistry, Vol. 1, Physical Methods of Organic Chemistry, Parts I and II, 2nd. Ed.—Edited By Arnold Weissberger.
10. Organic Chlorine Compounds—By Earnest H. Huntrez.
11. An Introduction to Organic Chemistry—By Rogers Williams and Lewis F. Hatch.
12. Synthetic Methods of Organic Chemistry, Vol. II—By W. Theitheimer.
13. A Century of British Chemistry—By Dr. F. Sherwood Taylor.
14. The Economic Prospects of Chemical Industries in India—By Sri A. K. Madan, M. Sc. (Tech.).
15. Practical Application of Recent Lac Research, New Edition—By H. K. Sen and M. Venugopalan.
16. Synthetic Petrol—By S. L. Bhatia.
17. Immunity Bulletin, Capt. N. N. Dutta Commemorial Volume—By Bengal Immunity Research Institute.

During the year the following books have been received for review :

1. Gmelins Handbuch der Anorganischen Chemie, 8 Auflage, System No. 18, 1949.
2. Gmelins etc.—8, Auflage, System No. 63, 1949.
3. High Polymeric Chemistry—By W. S. Penn.
4. Modern Plastics, 2nd Edition—By Harry Barron.

5. Immunity Bulletin, May 1947—April 1948, (B. I. R. I.)
6. Electron Microscopy—By W. G. Wyckoff.
7. Technique in Organic Chemistry—Vol. 1, (Physical Methods Part II) 2nd Ed.—By A. Weissberger.
8. Synthetic Petrol—By S. L. Bhatia.
9. Frontiers in Colloid Chemistry—By R. E. Burk & O. Grummit.
10. India and Science—By M. Mehrotra.
11. Biophysical Research Methods—By Fred M. Uber.
12. Fortschritte der chemischen Forschung—1 Band, 1/2 Heft.
13. Immunity Bulletin—Capt. N. N. Dutta Commemoration Vol., April, 1950.
14. The Chemistry of Heterocyclic Compounds—By F. G. Mann.
15. Technique in Organic Chemistry—Vol. 3—By A. Weissberger.
16. A Century of British Chemistry—By F. Sherwood Taylor.
17. Report on the working Trustees of the Lady Tata Memorial Trust, 1933—1947.
18. Festschrift Tillagnad—By J. Arvid Hedvall.
19. J. C. Bose's Plant Physiological Investigations in relation to modern biological knowledge—By D. M. Bose.
20. Textile Testing, 2nd Edition—By John H. Skinkle.
21. The Economic Prospects of Chemical Industries in India—By A. K. Madan.
22. Practical Applications of recent Lac Research—By H. K. Sen & M. Venugopalan.
23. Kunstleder Handbuch—By Walter M. Munzinger.
24. Melting and Solidification of Fats and Fatty acids series—Fats and Oils—By Alton E. Baily.
25. Chemical Society, Annual Report, Vol. XLVI, 1949.
26. Organic Chemistry, Second Edition—By Fieser & Fieser.
27. Colorimetric Determination of Traces of Metals, 2nd Ed., Chemical Analysis, Vol. 3—By E. B. Sandell.

### COMMITTEES & SUB-COMMITTEES

During the year the following Committees and Sub-Committees have been appointed :

- (1) A Committee for considering the suggestion of Dr. U. P. Basu for the formation of several divisions, e.g., Agriculture & Food, Analytical, Gas & Fuel etc., within the Society for each division.
- (2) A Sub-Committee to report regarding the supply of extra reprints.

### MEETINGS & LECTURES

During the year under review 9 meetings of the Council and 6 Ordinary meetings of the Society were held.

Prof. Sir Robert Robinson, M. A., D. Sc., LL. D., P. R. S., N. L., addressed the Fellows of the Society on 12th January, 1950 about "Recent Investigations in Dyson Perrins' Laboratory".

Dr. R. R. Williams of the Research Corporation of U. S. A. kindly consented to deliver an address to the Fellows of the Society on the 'Chemistry of Vitamin B<sub>1</sub>' on 15th December, but the meeting had to be cancelled on account of the sad demise of Sardar Vallabhbhai Patel on that day.

#### ACKNOWLEDGEMENTS

The Council wishes to record its sincere appreciation and cordial thanks to the authorities of the Science Congress, Bangalore, for extending their generous co-operation in holding its Annual functions.

Thanks of the Council are also due to the members of various Committees, Sub-Committees, Board of Associate Editors, Editorial Correspondents and Referees for their honorary services.

The Secretary is thankful to the staff of the Society for their kind help and co-operation in the management of the affairs of the Society.

# THE INDIAN CHEMICAL SOCIETY, BOMBAY BRANCH

## *Twenty-fifth Annual Report and Statement of Accounts of the Bombay Branch*

In the year under review the following meetings were held :

17- 2-50	Dr. A. B. Kulkarni	Synthesis of 5-hydroxy coprostane.
28- 8-50	Dr. N. G. Magar	Auto-oxidation of fats.
8-12-50	Dr. G. R. Gogate	Chemistry of glutaconic acids.
15-12-50	Dr. B. N. Ghosh	Bond dissociation energy of organic halides.

A social meeting was held on 1-9-50 to give a send-off to Dr. R. C. Shah.

The twenty-fifth annual general meeting of the branch was held on 19th December, 1950, at which a condolence resolution was passed to mourn the death of Sardar Vallabhbhai Patel.

The following Office-bearers were elected for the ensuing year :

President :	Dr. G. P. Kane
Vice-Presidents :	Dr. G. V. Jadhav Prof. P. M. Barve
Treasurer :	Dr. V. M. Bhawe
Secretaries :	Prof. A. N. Kothare Dr. M. B. Kabadi
Members :	Prof. S. M. Mehta Mr. G. C. Mitter Dr. Amin Tyabjee Dr. S. M. Sethna Dr. V. M. Thakur.

Prof. S. M. Mehta, the President of the branch, delivered a Presidential Address wherein he pointed out the potentialities and need of research in Inorganic Chemistry and discussed in detail the new method of recovery of Titania and importance of metallurgy of Titanium.

**Statement of Accounts**

<i>Receipts.</i>		<i>Expenditure.</i>	
Balance from the last year	Rs. 142/7/-	Stationery & Postage	Rs. 13 0 0
		Typing	Rs. 5 0 0
		Press announcements	Rs. 19 2 0
		Menials	Rs. 3 0 0
		Balance	Rs. 102 5 0
		<b>TOTAL</b>	<b>Rs. 142 7 0</b>

A. N. Kothare  
M. B. Kabadi  
Jt. Hon. Secretaries.

{ V. M. Bhawe  
Treasurer.

{ S. M. Mehta  
President.

## INDIAN

## RECEIPTS AND PAYMENTS ACCOUNT FOR THE PERIOD

## RECEIPTS

				Rs. As. P.	Rs. As. P.
Fellows	...	...	...	7,373 8 9	
Subscribers	...	...	...	6,015 5 0	13,388 13 9
Advertisement	...	...	...		2,282 10 0
Sale proceeds of Journal and Reprints	...	...	...		3,527 11 0
Donation	...	...	...		8,350 0 0
Associate Members	...	...	...		146 0 0
Interest	...	...	...		459 6 0
Miscellaneous (Sale of old waste papers)	...	...	...		34 0 0
					<u>28,183 8 9</u>
Loan refund to General Fund	...	...	...		25 4 0
Sir. P. C. Ray Memorial Fund	...	...	...		7 319 0 0
Opening Balance :					
Advance to Secretary for attending Annual General Meeting	...	...	...	100 0 0	
Cash in hand	...	...	...	50 0 0	150 0 0
Cash at Central Bank	...	...	...	4,247 15 0	
Cash at Grindlays Bank	...	...	...	9,345 1 4	
				<u>13,593 0 4</u>	
Less Cheques not cashed	...	...	...	201 12 0	
				<u>13,391 4 4</u>	
Add Cheques not audited	...	...	...	64 4 0	13,455 8 4
				<u>Total Rs.</u>	<u>49,138 5 1</u>

J. M. DAS GUPTA

				Rs. As. P.	Rs. As. P.
Opening Balance	...	...	...	14 8 0	129 12 8
Interest audited	...	...	...	14 8 0	29 0 0
				<u>Total Rs.</u>	<u>158 12 8</u>



**CHEMICAL SOCIETY**

FROM DECEMBER 16, 1949 TO DECEMBER 15, 1950.

**PAYMENTS**

			Rs. As. P.	Rs. As. P.
Salaries & Wages	...	...	6,898 6 0	
D. A. & S. A.	...	...	2,220 0 0	9,118 6 0
New Appointment, Increment	...	...		2,000 0 0
Provident Fund	...	...		322 8 0
Paper	...	...		5,361 9 9
Printing	...	...		6,483 5 3
Postage	...	...		1,950 2 9
Binding	...	...		865 15 6
Block-making	...	...		965 14 6
Stationery	...	...		367 7 3
Travelling	...	...		253 5 0
Miscellaneous	...	...		527 5 0
Purchase of Journal	...	...		510 15 0
Bank Charges	...	...		111 12 9
				<u>28,838 10 9</u>
Loan from General Fund	...	...		120 0 0
History of Chemistry	...	...		218 9 0
Provident Fund Loan refund	...	...		220 0 0
Transfer to Sir P. C. Ray Memorial Fund	...	...		7,319 0 0
<b>Closing Balance :</b>				
Cash in hand	...	...		50 0 0
Cash at Central	...	...	7 145 3 9	
Cash at Grindlay	...	...	5,879 7 7	
			<u>13,024 11 4</u>	
Less Cheques not cashed	...	...	652 10 0	12,372 1 4*
Balance includes Rs. 7,334/7/- for History of Chemistry Fund			<u>Total Rs.</u>	<u>49,138 5 1</u>

**MEMORIAL FUND**

			Rs. As. P.
By Charges as per P. Book	...	...	0 9 6
Balance	...	...	158 3 2
			<u>Total Rs.</u>
			158 12 8

The securities in J. M. Das Gupta Memorial Fund  
at Grindlays Bank are 3% Conv. Loan Rs. 1,000-0-0

INDIAN  
EMPLOYEES PROVIDENT FUND

Opening Balance			Rs.	As.	P.	Rs.	As.	P.
Cash at S. B. Pass Book	...	...	5,819	3	6			
Amount not realised	...	...	147	8	0	5,966	11	6
Employees subscriptions	...	...	322	8	0			
Society's contribution	...	...	322	8	0	645	0	0
Interest realised as per Pass Book						61	9	0
Loan refund						220	0	0
			TOTAL Rs	...		6,893	4	6

**P. C. RAY**

		Rs.	As.	P.	Rs.	As.	P.
Interest realised as per Pass Book on 3% Loan Rs. 1,500	...	...	44	8	0		
" " 32,000	...	...	957	8	0		
" " 8,500	...	...	254	0	0		
						1,256	0 0
Deposit	...	...				7,319	0 0
Opening Balance	...	...				2070	0 5
TOTAL Rs	...	...				10,645	0 .5

1. 2. 3. 4.

- 3 -

100 100 100

2. *Amphispiza bilineata* (Aud.)

U.S. Department of State  
Washington, D.C. 20520

**CHEMICAL SOCIETY****AND SAVINGS BANK ACCOUNTS**

	Rs.	As.	P.	Rs.	As.	P.
Loan for Provident Fund	...	...	...	150	0	0
Bank charges as per Pass Book	...	...	...	0	9	6
Balance as per Pass Book	...	...	...	6,668	15	0
Amount not credited	...	...	...	73	12	0
				<u>6,742</u>	<u>11</u>	<u>0</u>
<b>TOTAL Rs.</b>	...	...	...	<b>6,893</b>	<b>4</b>	<b>6</b>

**MEMORIAL FUND ACCOUNT**

	Rs.	As.	P.	Rs.	As.	P.
To cost of making dies & supplying 500 copper Badges, 2 pieces Bronze Medals	...	...	...	425	0	0
To cost of Printing Sir P. C. Ray Memorial Fund appeal & Donors list	...	...	...	93	11	6
To conveyance expenses & flower for Sir P. C. Ray day	...	...	...	23	2	6
Postage to send Notice for Sir P. C. Ray Memorial Lecture	...	...	...	30	0	0
To cost of printing invitation Cards, conveyance, flowers, etc. for Aug. 2nd Lecture	...	...	...	36	13	0
To cost of supplying Bronze Medal with Case	...	...	...	25	0	0
Honorarium for Lecturer	...	...	...	500	0	0
Bank Charges	...	...	...	4	4	0
				<u>1,137</u>	<u>15</u>	<u>0</u>
Closing Balance	...	...	...	9,507	1	0
<b>TOTAL Rs.</b>	...	...	...	<b>10,645</b>	<b>0</b>	<b>5</b>

The securities in the Sir P. C. Ray Memorial Fund  
At Imperial Bank are 3% Loan Rs. 42,000/-

We have examined the above receipts and Payments Accounts with books and vouchers of the Society and its Funds and in our opinion they are correct. We have also verified the Certificates of the Society's Bank at Grindlays showing the Securities Rs. 15,000/- and National Savings Certificates Rs. 3,500/- and at Imperial Bank of India, National Savings Certificates of the value of Rs. 16,500/-.

CALCUTTA  
The 21st December,  
1950.

P. C. Nandi  
A. B. Gupta  
Chartered Accountant.

Hony. J. K. Choudhury  
Auditors. Hony. Treasurer.

## APPENDIX A

### LIST OF EXCHANGE JOURNALS

1. Acta Chemica Scandinavica.
2. Analytical Chemistry.
3. Analyst.
4. Advancement of Science.
5. American Journal of Science.
6. Annales De La Association Quimica Argentina.
7. Annals des Falsifications et des Fraudes
8. Archives des Sciences.
9. Australian Journal of Experimental Biology and Medical Science.
10. Biological Bulletin.
11. Brewers Digest.
12. British Abstracts (B. I, II & III).
13. British Coal Utilisation Research Association (Monthly Bulletin & Quarterly Gazette).
14. British Rayon and Silk Journal.
15. Current Science.
16. Chemical Age.
17. Chimie & Industrie.
18. Chemical Reviews.
19. Canadian Journal of Research.
20. Dissertations of the University of Basel.
21. Endeavour.
22. Glass.
23. Helvetica Chimica Acta.
24. Industrial and Engineering Chemistry, U. S. A.
25. Indian Journal of Pharmacy.
26. Indian Journal of Physics.
27. Industria Y Quimica.
28. Indian Journal of Medical Research.
29. Indian Farming.
30. Indian Journal of Agricultural Science.
31. Indian Soap Journal.
32. Il Farmaco Scienza de Tecnica.
33. Indian Trade Journal.
34. Journal of the Chemical Society, London.
35. Journal of the American Chemical Society.
36. Journal of the Society Chemical Industry.
37. Journal of Chemical Education.
38. Journal of Scientific & Industrial Research.
39. Journal of the American Oil Chemist's Society.
40. Journal of the Franklin Institute.
41. Journal and Proceedings of the Royal Society of New South Wales.

42. Journal of the American Pharmaceutical Association (Pr. Pharm. & Sc. Edu.)
43. Journal of the University of Bombay.
44. Journal of the Society of Dyers & Colourists.
45. Kolloid Zeitschrift.
46. Llyodia.
47. Memoirs de la Real Academia de Ciencias Y Artes de Berce'lona.
48. Manufacturer.
49. National Bureau of Standards-Technical News Bulletin.
50. Nachrichten von der Akademie der wissenschaften Zu Göttingen, Mathematisch-Physikalische Klasse.
51. Proceedings of the Indian Academy of Sciences.
52. Proceedings of the National Institute of Sciences of India.
53. Pharmaceutical Journal.
54. Proceedings of the Royal Society of Edinburgh.
55. Proceedings Koninklijke Nederlandsche Akademie Van Wetenschappen, Amsterdam.
56. Proceedings of the Leeds Philosophical and Literary Society.
57. Proceedings of the Cambridge Philosophical Society.
58. Proceedings of the National Academy of Sciences, U. S. A.
59. Paint Technology.
60. Physica.
61. Revue De L'Institut Fransais Du Petrole et Annales des Combustibles Liquides.
62. Reprints-Journal of the Institute of Metals, London.
63. Records of the Geological Survey of India.
64. Science and Culture.
65. Scientific Agriculture.
66. Science of Engineering, India.
67. Scientific Proceedings of the Royal Dublin Society.
68. Suomen Kemistilehti.
69. Tropical Agriculture, Trinidad.
70. Transactions of Chalmers University of Technology, Gothenbergh, Sweeden.
71. UNESCO Bulletin for Libraries.
72. Vierteljahrsschrift Der naturforschenden Gesellschaft in Zürich.
73. Texas reports on Biology and Medicine.
74. Revue Internationale des Industries Agricoles.
75. Chemische Berichte.
76. Collected Papers from the Faculty of Science, Osaka Imperial University
77. Annalen der Chemie.
78. AFINIDAD.
79. Mysore Information Bulletin.
80. British Abstracts—C.
81. Journal of the Pharmaceutical Society of Japan.
82. Dissertation Uppsala.
83. Arkiv for Kemi.
84. Bulletin Des Societies Chimiques Belges.
85. Proceedings of the Royal Society of Victoria.
86. Bulletin of the Tokyo Institute of Technology

87. Bulletin Analytique.
88. Sitzungberichte der Deutschen Akademie der Wissenschaften Zu Berlin.
89. F. A. O. Bulletin.
90. O. S. R. Publications and News.
91. Gmelin Institut—Hanbuch.

## APPENDIX B

### *List of Fellows admitted during the year 1950.*

1. Dhanonjoy Nosipuri, Esq., M. Sc., Research Scholar, 171, Lower Circular Road, Calcutta-14.
2. Sukumar Bose, Esq., M. Sc., Professor of Chemistry, Ripon College, Calcutta ; 5, Abhoy Mitra Street, Calcutta.
3. Radhapada Das, Esq., M. Sc., P 7, Motizil Avenue, Dumdum.
4. Siddhheswar Banerjee, Esq., M. Sc., Research Assistant, Chemical Laboratory, Presidency College, Calcutta.
5. Jagadish Lal Narula, Esq., M. Sc., Professor of Chemistry, Ramjas College, Delhi.
6. Rajendra Pal Singh, Esq., M. Sc., Lecturer in Chemistry, University of Delhi, Delhi.
7. Prabhat Ranjan Pal, Esq., M. Sc., Dept. of Applied Chemistry, University College of Science, Calcutta.
8. Guruprasad Basu Chaudhury, Esq., M. Sc., 44, Chatterjee Para Lane, Bantra, Howrah.
9. Ram Chandra Sharma, Esq., Managing Director, Derivatives Factory, The Himal Miners' Syndicate Ltd., Paknajor, Kathmandu, Nepal.
10. Sivaprasad Bhattacharya, Esq., M. Sc., Chemical Laboratory, Presidency College, Calcutta.
11. Dewan K. S. Puri, Esq., B. Sc., Govt. Consulting Expert to Patiala Union Govt., Puri Buildings, Patiala.
12. Mukul Kumar Bose, Esq., M. Sc., 3/2, Sham Bose Road, Calcutta-27.
13. Bhola Nath, Esq., M. Sc., Lecturer, Shia College, Lucknow.
14. Piyus Kanti Chaudhury, Esq., M. Sc., Standard Pharmaceutical Works Ltd., 67, Dr. Sures Sarkar Road, Entally, Calcutta.
15. Dr. Jamuna Dutt Tewari, D. Sc., Lecturer, Chemistry Department, Allahabad University, Allahabad.
16. Rabindranarayan Ganguly, Esq., M. Sc., B. L., Professor of Chemistry, R. G. Kar Medical College, Calcutta.
17. Biswanath Banerjee, Esq., M. Sc., Calcutta University Library, Calcutta.

18. Dr. Ashwinkumar Madhavlal Trivedi, M. Sc., Ph. D., (Edinburgh) L. D. Arts College & M. G. Science Institute, Naorungpura, Ahmedabad.
19. Gopal Chandra Mukherjee, Esq., M. Sc., Works Inspection Officer, Ammunition Factory, Indian Ordnance Service, Kirkee, Poona.
20. Sukumar Banerjee, Esq., M. Sc., 60, Joy Mitter Street, Calcutta-5.
21. Rev. Lourdu M. Yeddnapalli, S. J., Ph. D., D. Sc., M. A., Professor and Head of Chemistry Dept., Loyola College, Cathedral P. O., Madras-6.
22. Pritipal Singh Sodhi, Esq., M. Sc., Professor of Chemistry, S. M. College, Chandausi (Dist. Moradabad).
23. James William McBain, F. R. S., Director, National Chemical Laboratory, Poona-5.
24. Dr. C. M. Mehta, M. Sc., Ph. D., Baroda College, Baroda.
25. Dr. Jnanendra Nath Chatterjee, M. Sc., D. Phil. (Oxon), The Chemical Laboratory, Science College, Patna.
26. J. R. Guha, Esq., B. Sc., A. I. I. Sc., Asstt. Development Officer (Drugs), Chemicals Directorate, D. G. I. & S., Shajahan Road, New Delhi.
27. Birendra Nath Dutta, Esq., M. Sc., 78B, Manicktolla Street, Calcutta-6.
28. Dr. M. A. Saboor, M. Sc., Ph. D., A. R. I. C., Deputy Director of Industries (Research), West Bengal Govt., 7, Council House Street, Calcutta.
29. Madan Lall Khullar, Esq., M. Sc. (Chem. Eng.), 6648, Fifth Avenue, Pittsburgh 6, Pa., U. S. A.
30. Sisir Kumar Ganguly, Esq., M. Sc., 39, Lower Circular Road, Calcutta-16.
31. Cedric Sudhir Shaw, Esq., M. Sc., Chemistry Department, University of Allahabad, Allahabad.
32. Asoke Kumar Bose, Esq., M. Sc., 28/1, Nilmony Mitter Street, Calcutta-6.
33. Kumar Krishna Chatterji, Esq., M. Sc., Lecturer in Chemistry, Surendra Nath College, 13F, Gour Sundar Sett Lane, Cossipore, Calcutta.
34. Mr. Bonino Giovanni Battista, Professor of Chemistry and Director of Institute, Bologna (Italy) Istituto Chimico Giacomo Ciamician dell'Universita—Via Selmi 2.
35. Anil Kumar Dey, Esq., M. Sc., Chemical Engineering Dept., C. E. T. Bengal, P. O. Jadavpur College, Calcutta-32.
36. Narwani Chubarmal Suritram, Esq., M. Sc., 18, Shrimali Society, Naurangpura, Ahmedabad-9.
37. Natverlal Madhavlal Sheth, Esq., M. Sc., Jagmal's Pole, Bank Road, Baroda.
38. Arun Banerjee, Esq., M. Sc., P, 18, Mission Row Extension, Calcutta.
39. Debabrata Sen, Esq., M. Sc., 62, Hindusthan Park, P. O. Rash Behari Avenue, Calcutta.
40. Vikramaditya Bhargava, Esq., M. Sc., Behind Arya Samaj Naya Bazar, Lashkar, Gwalior.

41. Subash Kumar Ghosh, Esq., M. sc., Lecturer in Chemistry, Presidency College, 241-B, Bagmari Road, Calcutta—11.
42. Advani Ramchand Dialmal, Esq., M. sc., Senior Professor of Chemistry, S. B. Garda College, Navsari.
43. Dr. Durgadas Lahiri, M. sc., Ph. D. (Sheffield), Department of Applied Chemistry, 92, Upper Circular Road, Science College, Calcutta—9.
44. K. Sundararaman, Esq., B. sc., 86, Butterworth Road, Teppakulam P. O., Tiruchirapalli.
45. Monisha Bose, M. sc., Professor of Chemistry, Lady Brabourne College, Calcutta, P. 35, Central Avenue, Flat No. B-3, Calcutta.
46. N. Subramanyan, Esq., M. sc., Chemist Mettur Chemical & Industrial Corporation Ltd., Mettur Dam R. S.
47. Ajit Kumar Mukhopadhyay, Esq., M. sc., Research Student, Pure Chemistry, University of Calcutta, 26, Ramesh Mitra Road, Calcutta—25.
48. Dr. Gauri Sankar Misra, M. sc., Ph.D., (Lond.), Lecturer in Chemistry, Lucknow University, Lucknow.
49. Sushil Kumar Mukherjee, Esq., M. sc., Research Student, Indian Association for the Cultivation of Science, Calcutta, 47A, Raja Dinendra St. Calcutta—9.
50. Dr. G. Gopala Rao, D. sc., Professor of Chemistry and Head of the Department of Chemistry, Andhra University, Waltair.
51. Mr. John David Plett, M. A. (Cantab.) B. sc., (Lond.), A. R. I. C., C/o. Imperial Chemical Industries (India) Ltd., 18, Strand Road, Calcutta—1.
52. Jaswant Rai Sarin, Esq., B. sc., 4, Laxman Bagh, Nawabganj, Kanpur.
53. Asoke Kumar Mukherjee, Esq., M. sc., 25-1B, Garpar Road, Calcutta—9.
54. Dr. Jashanmal Jiwatram Azad, B. A., M. H. S. L. (Lond.), Degan Homoeo Hospital, C/o. 494-1, Napier Town, Jubbulpore.
55. Dr. Daulatraj Makanji, M. sc., Ph. D., Karnatak College, Dharwar.
56. Mr. R. M. Fraser Thomson, C/o. Imperial Chemical Industries (India) Ltd., 62A, Free School Street, Calcutta.
57. B. L. Pandharipande, Esq., B. sc., B. sc. (Tech.), C/o. Shri P. R. Deopujari, Pleader, Balaghat, C. P.
58. Mr. C. D. Allen, B. sc. (Dublin), A.R.I.C., Scottish Church College, 4, Cornwallis Street, Calcutta—6.
59. Prohlad Kumar Das, Esq., B. sc., 365, Circular Road, Howrah, P. O. Botanic Garden, Bengal.
60. Ram Sahai Saxena, Esq., M. sc., Head of the Chemistry Department, Herbert College, Kotah (Rajasthan).
61. Dharam Bal Parihar, Esq., M. sc., Lecturer in Chemistry, Department of Chemistry, University of Delhi, Delhi.
62. Dr. Rohini Kanta Barua, M. sc., Ph. D., Asst. Professor of Biochemistry, Assam Medical College, Khaliamari, Dibrugarh, Assam.



63. Amallesh Chatterjee, Esq., M. Sc., Chemist, B.C.P.W. Ltd., 1, S. K. Sarbadhikary Lane, Calcutta—10.
64. Vyas Vasudev Ambalal, Esq., M. Sc., Prof. of Chemistry and Head of the Chemistry Dept., Dharmendrasinhji College, Rajkot (Saurashtra).
65. Kailash Chandra Mathur, Esq., M. Sc., Lecturer, Dept. of Chemistry, S. M. College, Chandausi, Dist. Moradabad (U.P.)
66. Krishna Chandra Joshi, Esq., M. Sc., Senior Analyst (Food), Public Analyst Dept., Chemistry Block, Lucknow University, Lucknow.
67. Paresch, Chandra Das, Esq., M. Sc., Indian Jute Mills Association Research Institute, 16, Old Court House Street, Calcutta.
68. P. Thomas Oommen, Esq., B. Sc., B. Pharm. (B. H. U.), 39A, Perambur High Road, Madras—11.
69. Dr. Dharendra Kumar Chaudhuri, M. Sc., Ph. D. (Cantab), Biochemistry Laboratory, Department of Applied Chemistry, University College of Science, Calcutta.
70. Sri Dhirendralal Nandi, Lecturer in Chemistry, Itachuna College, Hoogly (Dist.), 5-4, Cornfield Road, Ballyganj, Calcutta—19.
71. Deva Das Mukherjee, Esq., M. Sc., Research Assistant, Chemistry Dept., Lucknow University, Lucknow.
72. C. P. Gopinath, Esq., B. Sc., Chemist, Bharath Laboratories, Arvambakam, "Ramola", 44, Spur Tank Road, Egmore, Madras—5.
73. A. K. M. Pillai, Esq., B. A., M. Sc., A.I.R.I. (London). Deputy Director, U.S.T. (Govt. of India), 6, Esplanade East, Calcutta. (Permanent Address :- Appium House, Quilon, Travancore.)
74. Budhadev Sen, Esq., M. Sc., Lecturer in Analytical Chemistry, Chem. Eng. Department, College of Engineering & Technology, Jadavpur, Bengal, P 75B, Lake Road, Calcutta—29.
75. Dr. Pratul Nath Sen Gupta, M. Sc., D. Phil. (Cal.), A. R. I. C., Biochemist, Department of Anthropology, Govt. of India, Indian Museum, Calcutta.
76. Dr. Dharma Brata Das, B. Sc., M. Sc., Ph. D. (Leeds), A. R. I. C., 88, Moyradanga Road, Flat 8C, Barnagore, Calcutta—36.
77. Mr. John Ferguson Wareham, B. Sc., (Hons.), A. R. I. C., Chief Chemist, Groups Laboratory, Jardine Henderson Ltd., Barnagore House, Calcutta.
78. Mrityunjay Kumar Mitra, Esq., B. Sc. 56/1B, Sreegopal Mullick Lane Calcutta.
79. Basant Lal Agrawal, Esq., Krishna College, Atrauli (Aligarh).
80. Sani Dass Rehan, Esq., M. Sc., C/o. M/s Bakshi Ram Harbus Lal, P. O. Shahkot, Dist. Jullunder, Punjab. (I).
81. Dr. Dharendra Nath Chaudhury, M. Sc., Ph. D. (Liverpool), A. R. I. C., Assistant Professor of Chemistry, G. B. B. College, Muzaffarpur, Bihar.

**Associate Members :**

1. Pramodechandra Laxmishanker Trivedi, Esq., M. Sc., Chemistry Dept., Royal Institute of Science, Mayo Road, Fort Bombay.
2. (Miss) Ragini Vithal Phadke, M. Sc., 4A, Siri Road, Malabar Hill, Bombay—6.
3. Mr. Sadashiv Ambadas Kulkarni, M. Sc., 18, 'Shri-Nivas', Prarthana Samaj Road, Vile Parle, Bombay—24.
4. Motiram Vishnool Shirsat, Esq., M. Sc., Dept. of Chemotherapy, Haffkine Institute, Parel, Bombay—12.
5. Sukhamoy Bhattacharya, Esq., B. Sc., Bengal Immunity Research Institute, 39, Lower Circular Road, Calcutta—16.
6. Ramesh Jagmohan Parikh, Esq., B. Sc., Institute of Science, Mayo Road, Fort, Bombay—1.
7. V. Thiagarajan, Esq., M. Sc., Fuels Laboratory Assistant, Staff Quarters, College of Engineering, Guindy, Madras—15.
8. B. R. Lakshmana Rao, Esq., M. Sc., Andhra University, Waltair.
9. D. S. N. Murthy, Esq., M. Sc., Chemistry Department, Andhra University, Waltair.
10. Ch. Venkataswarlu, Esq., M. Sc., Chemistry Department, Andhra University, Waltair.
11. B. Keshav Shenoy, Esq., B. Sc., Chemistry Laboratory, Engineering College, Guindy, Madras—15.
12. Sunil Kumar Siddhanta, Esq., M. Sc., 35/7, Puddupuker Road, Calcutta—20.
13. Ramesh Balvantrao Desai, Esq., B. Sc., C/o. B. M. Desai, 190, Khetwadi Main Road, Bombay—4.
14. Kshetra Prosad Sen Sarma, Esq., M. Sc., Lecturer in Chemistry, Narsinha Dutt College, Howrah, 151-3A, Musjid Bari Street, Calcutta.
15. Md. Alim Biswas, Esq., B. Sc., Dept. of Chemistry, Dacca University, Dacca, East Pakistan.
16. Sachindra Kumar Dutta, Esq., M. Sc., Chemical Laboratory, Darjeeling Government College, Darjeeling, Bengal.
17. Khirod Kumar Patnaik, Esq., M. Sc., Chemical Laboratory, Balasore College, Balasore, Orissa.
18. Tarakeswar Chakravarty, Esq., M. Sc., Chemical Laboratory, Krishnanagore College, Krishnanagore W. Bengal.
19. Kalyan Kumar Mukherjee, Esq., M. Sc., 26, Cantonment Road, Cuttack—1.
20. T. V. Satyamurthy, Esq., M. Sc., 5, Duraiswamy Road, Thyagaraya Nagar, Madras—17.
21. S. Swaminathan, Esq., M. Sc., 9, Duraiswamy Road, Thyagaraya Nagar, Madras—17.
22. Mahtab Chandra Rastogi, Esq., M. Sc., Lecturer in Chemistry, Chemistry Dept., Lucknow University, Lucknow.
23. Ram Dulary Srivastava, Esq., M. Sc., Chemistry Dept., Lucknow University, Lucknow.

24. Benoy Bhusan Bose, Esq., B. sc., (Dacca), C/o. Mr. D. K. Bose, Air India Ltd., Great Eastern Hotel, Calcutta.
25. Dattatrya Moreswar Kulkarni, Esq., B. sc., C/o. Chinchwadkar Pleader, 349B, Mangalwar Peth, Kolhapur City.
26. Om Prakash Bansal, Esq., M. sc., Agra University Research Scholar, 4, Nanlakha, Agra Cantt.
27. Sudhakar Gupta, Esq., M. sc., C/o. Dr. S. S. Guha Sircar, Chemical Laboratory, Ravenshaw College, Cuttack—3, Orissa.
28. Jyotirmoy Mitra, Esq., M. sc., C/o. Dr. S. S. Guha Sircar.
29. Mahmad Ismet Ali, Esq., M. sc., C/o. Dr. S. S. Guha Sircar.
30. Kazi Abdul Latif, Esq., M. sc., C/o. Dr. S. S. Guha Sircar.
31. Jamshed Sorabji Behrana, Esq. M. sc. C/o. Prof. C. S. Narwani, M. sc., 18, Shrimali Society, Navrangapura, Ahmedabad—9.
32. Madhav Gajanan Marathe, Esq., M. sc., Ranade Institute, Dept. of Chemistry, University of Poona. Poona—4.
33. M. Krishnamurti, Esq., M. sc., Department of Chemistry, University of Delhi, Delhi.
34. Ajoy Kumar Chaudhuri, Esq., M. sc., Chemical Laboratory, Presidency College, Calcutta—12.

# INDIAN CHEMICAL SOCIETY

92, UPPER CIRCULAR ROAD, CALCUTTA—9

Minutes of the 27th Annual General Meeting of the Indian Chemical Society held on Saturday, January 6, 1951, at 3 P.M. in the Chemical Section meeting room of the Indian Science Congress at Bangalore.

Dr. P. C. Guha—in the chair.

Before the proceedings commenced the Chairman referred to the loss sustained by the country by the death of Sri Aurobindo Ghosh and Sardar Vallabhbhai Patel. The following resolution was passed all the members standing and two minutes' silence was observed in memory of the departed.

*Resolved* that the Council records with deep sense of sorrow the irreparable loss to India of two of her eminent sons Sri Aurobindo Ghosh, sage and philosopher, and Sardar Vallabhbhai Patel, the great leader, patriot and statesman. The Society pays its respectful homage to the departed great.

1. The following nominations of the Office-bearers, four Members of the Board of Editorial Correspondents and 2 Hony. Auditors, made by the Council, and the results of the scrutiny of the ballot papers for the election of 6 Ordinary Members of the Council were announced by the Chairman.

## *Office-bearers :*

- (a) President —Dr. P. C. Guha
- (b) Hony. Secretary —Dr. D. Chakravarti
- (c) Hony. Treasurer —Dr. B. N. Ghosh

## *6 Ordinary Members of the Council :*

- |                    |                      |
|--------------------|----------------------|
| Calcutta—3.        | South India—1.       |
| Dr. U. P. Basu     | Dr. B. Sanjiva Rao   |
| Dr. B. C. Guha     | U. P.—1.             |
| Dr. S. R. Palit    | Dr. S. S. Deshapande |
| Bihar and Orissa—1 |                      |
| Dr. P. K. Bose     |                      |

## *4 Editorial Correspondents :*

- Dr. R. C. Shah
- Dr. R. D. Desai
- Dr. S. S. Joshi
- Dr. S. K. K. Jatkar

## *2 Hony. Auditors :*

- Mr. P. C. Nandi
- Mr. A. B. Gupta
- (Chartered Accountants).

The election of the Office-bearers, 4 Editorial Correspondents, 6 Ordinary Members of the Council, and 2 Hony. Auditors, as announced was unanimously carried.

2. The following Supplementary Budget for 1950 was adopted unanimously.

*Supplementary Budget for 1950*

				Receipt upto 30. 9. 50.	Budget 1950.
Receipt :				Rs.	Rs.
Fellows	...	...	...	6,053	6,000
Subscribers	...	...	...	4,279	6,000
Advertisement	...	...	...	1,731	2,500
Sale proc. of Journal & Reprints	...	...	...	2,929	1,500
Donation	...	...	...	8,159*	4,500
Interest	...	...	...	453	448
Associate Member	...	...	...	107	52
Institution of Chemists	...	...	...	...	1,000
Miscellaneous	...	...	...	25	...
				23,736	22 000

\*Rs. 3,000/- from Bengal Govt.

				Receipt upto 30. 9. 50	Budget 1950	Supplementary Budget for 1950
Expenses :				Rs.	Rs.	Rs.
Salaries & Wages	...	...	...	5,085	7,980	7,980
Dearness Allowance	...	...	...	1,665	2 220	2,220
New appointment, increment & leave	...	...	...	1,460	2,000	2,000
Provident Fund	...	...	...	241	400	400
Paper	...	...	...	3,983	4,000	5,500
Printing	...	...	...	4,410	5,000	6,500
Postage	...	...	...	1,269	1,300	1,500
Binding	...	...	...	564	600	950
Block-making	...	...	...	790	800	950
Stationary	...	...	...	295	300	400
Travelling	...	...	...	197	400	400
Miscellaneous	...	...	...	492	500	700
Branches	...	...	...	...	100	100
Purchase of Journal & UNESCO Book Coupon	...	...	...	380	250	350
Rental	...	...	...	...	170	170
Bank charges	...	...	...	...	150	150
				20,732	26,170	30,270

3. The Hony. Secretary read the Council's Annual Report for 1950.

Dr. W. V. Bhagwat moved that the Annual Report be adopted.

Dr. Satya Prakash seconded the motion which was carried unanimously.

4. Dr. W. V. Bhagwat moved that the Hony. Treasurer's audited statement of accounts of the Society for 1950 as circulated be adopted.

Dr. R. C. Shah seconded the motion which was carried unanimously.

5. Dr. R. D. Desai moved that the following Budget Estimate for 1951 as recommended by the Council be adopted :

*Budget Estimate for 1951*

	Actual upto 15. 12. 49	Budget 1950	Actual upto 15. 12. 50	Budget 1951
Receipts :	Rs.	Rs.	Rs.	Rs.
Fellows ... ..	7,090	6,000	7,373	7,000
Subscribers ... ..	6,544	6,000	6,015	6,000
Advertisement ... ..	3,336	2,500	2,282	2,000
Sale proc. of Journal & Reprints ... ..	5,173	1,500	3,527	2,000
Donation ... ..	9,700	4,500	8,350	8,000
Interest ... ..	448	448	459	450
Associate Members ... ..	96	52	146	100
Institution of Chemists ... ..	1,100	1,000	...	1,000
Miscellaneous ... ..	128	...	34	...
	33,615	22,000	28,186	26,550
	Actual upto 15. 12. 49	Budget 1950	Actual upto 15. 12. 50	Budget 1951
Expenses :	Rs.	Rs.	Rs.	Rs.
Salaries & Wages ... ..	7,206	7,980	6,898	9,696
Dearness Allowance ... ..	2,220	2,220	2,200	2,820
New appointment, revision of grades, increment and leave ... ..	199	2,000	2,000	4,000
Provident Fund ... ..	321	400	322	400
Paper ... ..	3,754	5,500	5,361	6,000
Printing ... ..	4,917	6,500	6,483	6,500
Postage ... ..	1,287	1,500	1,950*	2,000*
Binding ... ..	646	950	866	950
Block-making ... ..	802	950	965	950
Stationery ... ..	744	400	367	600
Travelling ... ..	149	400	253	400
Miscellaneous (including meeting expenses) ... ..	505	700	527	1,200
Branches ... ..	28	100	...	100
Purchase of Journal ... ..	...	350	510	500
Bank charges ... ..	139	150	111	182
Rental ... ..	...	170	...	182
	22,917	30,270	28,833	36,480

\*Including postage for the despatch of the back volumes of our Journal ordered for.

Dr. S. K. K. Jatkár seconded the motion which was carried unanimously.

6. The Chairman announced that the Acharya P. C. Ray Memorial Medal for 1950 be presented to Dr. J. C. Ghosh.

As Dr. J. C. Ghosh could not attend the meeting, the presentation was made *in absentia*.

Dr. W. V. Bhagwat moved that in future Acharya P. C. Roy Memorial Medal be presented on 2nd August when the Memorial lecture is delivered.

Dr. S. K. K. Jatkár seconded the proposal which was carried *nem/con*.

7. Dr. R. C. Shah moved that as recommended by the Council the Rules of the Society (Section VIII, clause 16 and Section XII) be amended as follows :

Rule—*Section VIII, clause 16*—"The office bearers shall be elected at the Annual General Meeting by the majority of Fellows, twenty forming a quorum. The nominations for election shall be made by the Council and announced at any Ordinary meeting at least four weeks before the Annual General Meeting".

Rule—*Section XII*—"The date of the Annual General Meeting shall be announced by the Council at least four weeks before the meeting and all notices of motion shall be received by the Secretary at least three weeks before the meeting".

Dr. S. K. K. Jatkár seconded the motion which was carried unanimously.

8. The letter from the Asst. Secretary, Department of Scientific and Industrial Research, Govt. of India, regarding the nomination of one or two representatives of Government of India on the Council of the Society was reconsidered.

After discussion in which Dr. A. N. Kappanna, Dr. B. Prasad, Dr. J. Gupta, Dr. N. Ghatak, Dr. W. V. Bhagwat and Dr. S. K. K. Jatkár and several other Fellows took part, the following resolution, expressing the general sense of the meeting, moved by the Chairman, was adopted :

Resolved that this meeting recommends for inclusion of an additional member (representative of the Government of India) in the Council, to be nominated by the Govt. of India from amongst the Fellows of the Society.

9. The change in the rates of Foreign subscriptions (Hard currency & Dollar area) which was circulated to the General Members for approval after being adopted at the Annual General Meeting at Poona, was accepted. The rates will be charged from all new parties and from old subscribers to whom notices of change have been sent through advertisement in some of our Journals of 1949.

Inland	{ Rs. 16/- (Fellows)
	{ Rs. 20/- (Main Journal)
	{ Rs. 24/- (For main Journal and Industrial & News Edition),

Foreign	{ Rs. 16/- (Fellows)
	{ Rs. 24/- (Main Journal)
	{ Rs. 30/- (For main Journal and Industrial and News Edition).
Hard Currency and Dollar Area	{ Rs. 21/- (Fellows)
	{ Rs. 32/- (Main Journal)
	{ Rs. 40/- (For main Journal and Industrial & News Edition).

Proposed by Dr. R. C. Shah and seconded by Dr. A. N. Kappanna.

10. The recommendation of the Council regarding the revision of the grade of the Asst. Secretary was considered.

After discussion in which several Fellows took part it was unanimously decided to refer back the matter to the Council and the Secretary was requested to convey to the Council the sense of the meeting that the post of Asst. Secretary and the Asst. Editor be amalgamated in one post with higher grade of pay and the post of one or two assistants may be created to do routine work, proof-reading etc.

11. The retiring President, Dr. J. N. Ray being unable to attend, the address was read by Dr. D. Chakravarti. Dr. A. N. Kappanna moved that the Presidential address be published in the main Journal of the Society and the motion was seconded by Dr. R. C. Shah and accepted.

With a vote of thanks to the Chair the meeting was dissolved.

D. Chakravarti  
*Hony. Secretary.*

P. C. Guha  
*Chairman.*



# INDIAN CHEMICAL SOCIETY

92, UPPER CIRCULAR ROAD, CALCUTTA—9

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## NOTICE

An Ordinary meeting of the Indian Chemical Society will be held on Friday, February 16 at 5 P.M. in the Chemistry Lecture Theatre, University College of Science, 92, Upper Circular Road, Calcutta. Fellows are requested to attend.

*February, 8, 1951.*

D. Chakravarti,  
*Hony. Secretary.*

## ITEMS OF BUSINESS

1. Admission of Fellows (Vide Appendix A).
2. Election of Fellows and Associate Members (Vide Appendix B).
3. Scientific business—The papers marked with an asterisk (\*) in the accompanying list of papers may be read in the meeting (Vide Appendix C).
4. Any other item that may be brought forward.

## APPENDIX A

*Names of the Candidates for admission who have paid their first subscription.*

1. Daleep Singh Deorha, Esq., M. Sc., Lecturer, Chemistry Department, Meerut College, Meerut.
2. Gopal Dass Tuli, Esq., M. Sc., Professor of Chemistry, Meerut College, Meerut.
3. Devendra Prasad Joshi, Esq., M. Sc., Chemistry Department, Meerut College, Meerut.
4. Inder Raj Gambhir, Esq., M. Sc., Lecturer in Chemistry, Meerut College, Meerut.
5. Dr. Shiam Sunder Joshi, D. Sc., Head of the Chemistry Department, Meerut College, Meerut.
6. S. Sultan Ali Jeofrey, Esq., M. Sc., Research Scholar, Agra College; C/o Prof. Ummed Ali, M. Sc., P. E. S. (Retd.), Vice-Principal, Sooce Katra, New Kotwali, Agra.
7. Indra Kishore Kacker, Esq., B. Sc. (Hons.), M. Sc., Central Laboratories for Scientific & Industrial Research, P. O. Jamai-Osmania, Hyderabad-Dn.
8. Damodar Prasad, Esq., M. Sc., Khabra Road, P. O. Muzaffarpur, Bihar, Chemical Laboratory G. B. B. College, Muzaffarpur.
9. Pradosh Ranjan Chatterji, Esq., M. Sc., Chief Chemist, Messrs Gillespie Chemical Industries, Calcutta, 3 F, Kirtibash Lane, P. O. Kalighat, Calcutta—26.
10. Dr. Dinkar Shripatrao Datar, B. A., M. Sc., A. I. I. Sc., Ph. D., Scientific Officer, Central Laboratories for Scientific and Industrial Research, P. O. Jamai-Osmania, Hyderabad-Dn.
11. Padmini Soni, M. Sc., "Wyngate", Simla-4.
12. Krishnapillai Viswanathan Nair Esq., M. Sc., Lecturer in Chemistry, Travancore University, Chemistry Dept, Lucknow University, Lucknow.
13. Harendra Nath Roy, Esq., M. Sc., A. R. I. C., Chief Chemist, Metal and Steel Factory, Ichapore, Indian Ordnance Department, 372/13, Russa Road, South, P. O. Tollygunj, Calcutta.
14. Chitta Ranjan Raha, Esq., M. Sc., 10/2, Musalmanpara Lane, Calcutta—9.

15. Dr. (Mrs.) Ashima Chatterjee (née Mookerjee), D. Sc., P. R. S., F. Sigma XI Fraternity (U. S. A.), F. Sigma Delta Epsilon (U. S. A.), M. Amer. Pharm. Assoc., University College of Science and Technology, 92, Upper Circular Road, Calcutta—9.

## APPENDIX B

### *Names of the Candidates for election.*

Fellows :

1. Pramodchandra Laxmishanker Trivedi, Esq., M. Sc., Asst. Lecturer in Micro-Analytical Chemistry, The Institute of Science, Bombay, Villar-Villa, Ghod Bunder Road, Santa-Cruz, Bombay—23.
2. Kompella Kameswara Sarma, Esq., M. Sc., Kymore Cement Works, P.O. Kymore, Via-Jukehi, G. I. P. Rly.
3. Ajay Kumar Chaudhuri, Esq., M. Sc., Research Scholar Govt. of India. Chemical Laboratory, Presidency College, Calcutta.
4. Dr. Sailaja Prasad Ghosh, M. Sc. (Pat.), Ph. D. (Dunelm). A. R. I. C., A. M. Inst. Science College, Patna—5.
5. Balai Chand Pathak, Esq., M. Sc., Applied Chemistry Department, University College of Science, 92, Upper Circular Road, Calcutta—9.
6. Saiyid Shamim-ahmad, Esq., M. Sc., Chemistry Department, Muslim University, Aligarh.
7. Bansidhar Vithaldas Mehta, Esq., M. Sc., Lecturer in Chemistry, Institute of Agriculture, Anand.
8. Dr. Bibhu Dass Banerji, M. Sc., D. Phil. (Allahabad) 14, Elgin Road, Allahabad.
9. Mohd. Mohsin Qureshi, Esq., Isshad Manzil, Morris Road, Aligarh.
10. Debabrata Sen, Esq., M. Sc., 47/4, South Sinthee Road, P. O. Cossipore, Calcutta—2.
11. Jyotsna Kumar Roy, Esq., M. Sc., Research Scholar, Calcutta University, 11B, Nandan Road, Calcutta—25.
12. Provas Kumar Dutta, Esq., M. Sc., Research Scholar, I. A. C. S. (Calcutta), Grand Trunk Road, Bhadrakali, P. O. Uttarpada, Dist. Hooghly.
13. Anantrao Narayanrao Godbole, Esq., M. Sc., Dr. Joshi's Building, Dandia Bazar, Baroda.
14. Dr. Jaysukhlal Ranchoddas Merchant, M. Sc., Ph. D., 333, Shri Nivas, Sandhurst Road, Bombay—4.

15. Vivekananda Bhatt M., Esq., B. Sc., A. I. I. Sc., Research Assistant, Dept. of Organic Chemistry, Indian Institute of Science, Bangalore—3.
16. M. Raghavan, Esq., B. Sc. (Hons.), M. A., A. I. I. Sc., Research Asst., Dept. of Organic Chemistry, Indian Institute of Science, Bangalore—3.
17. Akhil Chandra Ray, Esq., B. Sc. (Hons.), A. I. I. Sc., Research Asst., Dept. of Organic Chemistry, Indian Institute of Science, Bangalore—3.
18. Satya Sobhan Guha, Esq., M. Sc., Research Asst., Dept. of Organic Chemistry Indian Institute of Science, Bangalore —3.
19. Paresh Ranjan Gupta, B. Sc., A. I. I. Sc., Organic Chemistry Laboratory, Indian Institute of Science, Bangalore—3.
20. A. Vasudeva Kamath, Esq., M. Sc. (Tech), Research Asst., Dept. of Organic Chemistry, Indian Institute of Science, Bangalore—3.
21. Kaja Linga Murty, Esq., M. Sc., Main Road, Peddapuram, East Godvari Dt.
22. Ramchandra Laxman Khare, Esq. M. Sc., B12, Hostel, Indian Institute of Science, Bangalore—3. (Home Address) C/o L. J. Khare, M. A., L. L. B., Pleader, Daryapur (Behar), M. P.
23. Kadambi Narsimha Moorthy, Esq., M. Sc., Central Laboratories for Scientific & Industrial Research, Hyderabad-Dn.

Associate Members :

1. Jagadish Shankar Shukla, Esq., M. Sc., Research Scholar, Department of Chemistry, Lucknow University, Lucknow.
2. Jitendra Laxmidas Amin, B. Sc. (Agri.) Hons., Demonstrator in Chemistry, B. A. College of Agriculture, Anand. (B. B. & C. I. Rly.)
3. Jiban Kumar Chakravarti, Esq., M. Sc., Chemical Laboratories, Presidency College, Calcutta.
4. P. Sankar Rao, Esq., B. Sc. (Tech.), C/o Sri P. V. Rama Rao, B. A., B.L., Advocate, Powerpet, Ellore (M. S. M. Rly.).
5. (Miss) Razia Osmani, M. Sc., Central Laboratories for Scientific and Industrial Research, P. O. Jamai-Osmania, Hyderabad-Dn.
6. Hamid Ahmed Khan, Esq., M. Sc., Central Laboratories for Scientific and Industrial Research, P. O. Jamai-Osmania, Hyderabad-Dn.
7. Eshwar Raj Saxena, Esq., M. Sc., Central Laboratories for Scientific and Industrial Research, P. O. Jamai-Osmania, Hyderabad-Dn.
8. Kartar Singh, Esq., M. Sc., National Chemical Laboratory, Poona,

## APPENDIX C

*List of papers communicated to the Society between 22nd November,  
1950 to 31st January 1951.*

- \*1. A comparative study of the equations of Huckel and Smoluchowski connecting electrokinetic potential with the cataphoretic and electro-endosmotic velocities.—By B. N. Ghosh and R. N. Roy Chowdhuri, Calcutta.
2. Analytical chemistry of zirconium. Part I. Benzoic acid.—By M. Venkataranian and Bh. S. V. Raghava Rao, Waltair.
3. Application of mixture law to rheochor. Part V. Ternary mixtures.—M. V. Subnis and W. V. Bhagwat, Indore.
4. Studies on the dependence of optical rotatory power on chemical constitution. Part XXXVI. The rotatory dispersion of phenyl, *o*-*m*- and *p*-tolyl-imino- and amino-camphor.—By Bawa Kartar Singh and Kartar Singh, Benares.
5. A note on corchorin, a bitter principle of corchorus capsularis. (Jute seeds).—By D. N. Choudhury and Paresh Chandra Dutta, Muzaffarpur.
- \*6. Quinoline derivatives. Part XVI.—By T. N. Ghosh and Amitabha Roy Choudhuri, Calcutta.
- \*7. Influence of phenols on phenol reagent. A quantitative treatment of the dependence of the reducing capacity of phenols, on the nature and position of the substituents on the phenol nucleus.—By N. Ray, Cal.
8. Analytical chemistry of zirconium. Part II. Cinamic acid.—By Ch. Venkataswarlu and Bh. S. V. Raghava Rao, Waltair.
- \*9. On biguanidino sulphones.—By U. P. Basu, K. R. Chandran and Achintya Kamal Sen, Calcutta.
10. Studies of the action of alcoholic alkali on *o*-hydroxy or *o*-acetoxy-chalkone dibromides. Part I. Synthesis of flavones and benzylidene coumarins.—By M. G. Marathe, Poona.
11. Studies of action of alcoholic alkali on *o*-hydroxy or *o*-acetoxy-chalkone dibromides. Part II. Synthesis of flavones and benzylidene coumarins.—M. G. Marathe, Poona.
12. Studies of action of alcoholic alkali on *o*-hydroxy or *o*-acetoxy-chalkone dibromides. Part III. Synthesis of benzylidene coumarins.—By M. G. Marathe, Poona.
13. Studies in Elbs persulphate oxidation. Part III. Further oxidations in the coumarin series and oxidation of 8-hydroxy-quinoline.—By V. J. Dalvi, R. B. Desai and Suresh Sethna, Bombay.

14. Extraction of potash from felspar. Part II. Reaction of felspar with calcium carbonate and calcium sulphate.—By Eshwar Raj Saxena and D. S. Datar, Hyderabad.
15. Interaction of hydroxy acetophenones and their derivatives and thionyl chloride in presence of finely divided copper. Part III. Preparation of 3:3-diacetyl-4:4-dihydroxy-6:6-dimethoxy-diphenyl thioether and its derivatives from phenol.—By G. V. Jadhav and J. R. Merchant, Bombay.
16. Synthetic Insecticides. Part II. Condensation of butyl chloral hydrate with hydrocarbons and halohydrocarbons. Synthesis of  $\alpha$ -bis-(aryl)- $\beta$ - $\beta$ - $\gamma$ -trichloro- $m$ -butanes.—By (Miss) Latika H. Dalal and R. C. Shah, Bombay.
17. Synthetic insecticides. Part III. Condensation of butyl chloral hydrate with phenol and its ethers. Synthesis of  $\alpha$ -bis-(aryl)- $\beta$ - $\beta$ - $\gamma$ -trichloro- $m$ -butanes.—By (Miss) Latika H. Dalal and R. C. Shah, Bombay.
18. Synthetic insecticides. Part IV. Condensation of butyl chloral hydrate with cresols, some dihydric and their methyl ethers. Synthesis of  $\alpha$ : $\alpha$ -bis-(aryl)- $\beta$ : $\beta$ - $\gamma$ -trichloro- $m$ -butanes.—By (Miss) Latika H. Dalal and R. C. Shah, Bombay.
19. Synthesis of piperidine derivatives. Part III.—By (Miss) Padmini Soni and G. S. Sidhu, Hyderabad.
20. Sol-gel transformation of the ferro and ferri cyanides of some metals. Part II.—By S. Sultan Ali Jeofrey and Abani K. Bhattacharyya, Agra.
- \*21. Plant alkaloids. Part II. *Coptis Teeta* Wall.—By R. Chatterjee, M. P. Guha and A. Chatterjee, Calcutta.
22. Condensations of aryl diazonium salts with reactive unsaturated compounds. Part IV. Action of aryl diazonium chlorides with  $\alpha$ -methyl acrylic acid.—By M. Krishnamurti and Kunj Behari Lal Mathur, Delhi.
23. Condensations of aryl diazonium salts with reactive unsaturated compounds. Part V. Action of aryl diazonium chlorides with bromo-maleic acid.—By Sain Dass Rehan and Kunj Behari Lal Mathur, Delhi.
24. Boiling points of normal paraffins. Yatendra Pal Varshni, Allahabad.
25. Coumarins from orcinol derivatives : Condensation of oracetophenone monomethyl ether with ethyl acetate, ethyl propionate and ethyl butyrate, and molecular rearrangement of oracetophenone diacetate and dibenzoate in presence of metallic sodium—By Sharad S. Pandit and Suresh Sethna, Bombay.
26. Conrad-limpach quinoline synthesis with various arylamines and ethyl benzoylacetate. Part I.—By S. A. Kulkarni, V. M. Thakor and R. C. Shah, Bombay.
27. Anodic oxidation of formate ion.—By A. N. Kappanna, and Bhanu Ramchandra Deoras, Nagpur.

- \*28. Jute seeds—*Corchorus olitorius*. The composition of oil *olitorius*. Part I.—By Jiban Kumar Chakravarti and Nirmal Kumar Sen, Calcutta.
29. Periodates of mercury.—Surjit Singh and Appar Singh, Dehra Dun.
30. Physico-chemical studies on the composition of complex metallic ferro and ferricyanides. Part X. Conductometric and thermometric studies on the composition of zinc ferricyanide.—By Harish C. Gaur and A. K. Bhattacharya, Agra.
31. Interaction of carbon monoxide and hydrogen under silent electric discharge : Production of formaldehyde. Part III. Influence of catalysts and other factors.—By R. H. Sahasrabudhey and S. M. Deshpande, Benares.
32. Physico-chemical studies on the composition of complex metallic ferro and ferricyanides. Part XII. Conductometric and thermometric studies on the composition of nickel ferricyanide —By Harish C. Gaur and Abani K. Bhattacharya, Agra.
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